2010

LIBRARY
Michigan State
University

This is to certify that the
dissertation entitled

DEVELOPMENT OF ACTIVE PACKAGING FOR COSMETICS AND STUDY OF THE MIGRATION OF OXYGEN SCAVENGER

presented by

Yangjai Shin

has been accepted towards fulfillment
of the requirements for the

Ph.D. degree in Packaging

Susan E. Selke
Major Professor's Signature

May 29, 2009
Date

MSU is an Affirmative Action/Equal Opportunity Employer

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.
MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE

5/08 K:/Proj/Acc&Pres/CIRC/DateDue.indd

DEVELOPMENT OF ACTIVE PACKAGING FOR COSMETICS AND STUDY OF THE MIGRATION OF OXYGEN SCAVENGER

By

Yangjai Shin

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Packaging

2009

ABSTRACT

DEVELOPMENT OF ACTIVE PACKAGING FOR COSMETICS AND STUDY OF THE MIGRATION OF OXYGEN SCAVENGER

By

Yangjai Shin

Active packaging systems have been developed to extend the shelf life of products because passive packaging systems cannot completely solve the problems of degradation due to oxygen dissolved in products or contained in the headspace in packages. One of the most commonly used techniques in active packaging is the sachet type of oxygen absorbing system composed of iron powder. However, the use of a sachet has been considered a safety problem in Europe due to migration from oxygen scavengers. Therefore, the overall objective of this research was to develop a multilayer film that could reduce the migration of the main components from iron based oxygen scavengers more than do sachets, and active packaging which could extend the shelf life of oxygen sensitive cosmetics containing retinol.

The active packaging rapidly reduced the oxygen concentration of the headspace compared with conventional packaging. It reached 0.0 % within 30 days and stayed lower than 0.1 % for 180 days from an initial value of 20.9 %, while conventional packaging remained near 10.0 % after 180 days stored at 23 ℃ and 65 % RH. In evaluating the shelf life of retinol in cosmetics, the concentration in the conventional packaging was rapidly reduced from 3,464 IU to 2,511 IU after 24 weeks stored at 23 ℃ and 65 % RH, while the concentration in the active packages remained over 3,000 IU after 24 weeks.

From SEM & EDS analysis, the main elements of the oxygen scavenger in the core layer of multilayer films were identified as iron, sodium and chloride. Quantitative

analysis of the migration of the main elements into various food simulants was conducted using atomic absorption (AA) spectrometry for both types of oxygen scavengers. For the sum of the main components ($NaCl+CaCl_2+Fe_2O_3$) for OS1 in 3 % acetic acid, the highest value among the food simulants was 2.322 mg/L, and for OS2 was 0.928 mg/L. These values were all much less than the EU limit for total migration of 60 mg/L (90/128/EEC). Throughout the observation of the migration behavior for the main elements by SEM & EDS, no migration of any of these main elements was detected in the inner layer adjacent to the core layer containing oxygen scavenger of multilayer films, but they could be observed from the seamed parting line in a tube. This means that the main elements of oxygen scavenger in the core layer of the OS films did not pass through the inner layer and did not contact the food simulants and cosmetic. Therefore, it is assumed that the migration detected was from the exposed seam in the tube or from the exposed edges of the core layer in the migration disks.

Copyright by

YANGJAI SHIN

2009

This dissertation is dedicated to the father's spirit of the departed, Sooyong Shin

AKNOWLEDGEMENTS

I would like to express my deepest heartfelt thanks to Dr. Susan E.M. Selke as my advisor for her educational and professional guidance, timely advice, and keen sense of humor.

I also would like to express my sincere appreciation to Dr. Bruce R. Harte, Dr. M. Rubino and Dr. Ilsoon Lee for their research guidance and support as committee members.

I am grateful to Dr. Kathryn G. Severin, Dr. Stanley L. Fleger, Dr. P. Nzokou and their research groups for all the great input and collaboration in this project. I would like to thank him for allowing me to use the lab equipment to finish the evaluation of migration test by atomic absorption spectrometer and SEM-EDS.

I would like to thank Mr. Yongwook Park, who is a CEO of E.SAENG Co., Ltd., for encouraging me to develop this project successfully, and both AMORE PACIFIC and E.SAENG company's members to develop the process technology of active packaging.

I would like to thank Dr. Joongmin Shin and Mr. Myoungil Kim for sharing their expertise and supporting me throughout my research, and Mr. D.W. Lee, Dr. J.K. Shim, and all colleagues in packaging industries.

Finally but not least, my deepest appreciation goes to my monther, Jongsun Lee, and my brothers, Hyunjae and Sungjae Shin, for their understanding and support. I thank

to my wife Yunyoung Huh for her loving support and continuous encouragement and two sons, Hanjung and Hyunjung Shin who understood me through the difficult times and while accomplishing my course work.

Yangjai Shin

East Lansing, MI

May 2009

TABLE OF CONTENTS

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Images in this dissertation are presented in color

Table **Page**

KEY TO ABBREVIATIONS OR SYMBOLS

Abbreviations

AA	Atomic absorption
AHAs	Alpha-hydroxy acids
ATRA	All-trans retinoic acid
AU	Area response
Aw	Water activities
BHA	Butylated hyalroxyanisole
BHA	Butylated hydroxytluene
CFSAN	Center for Food Safety and Applied Nutrition
CD	Cross direction
DEF	Difurylidene erythrito
DMA	Dimethyl anthracene
DMF	Dimethylformamide
DOT	Dioctyl phthalate
DRI	Dietary reference intake
DSC	Differential scanning calorimetry
HDPE	High density polyethylene
HFFS	Horizontal thermoform/fill/seal
ECCS	European community compliance statement

EGVM	Expert group on vitamins and minerals
ESFA	European Food Safety Authority
EMCM	Ethylene methylacrylate cyclohexenyl methyl acrylate
EVA	Ethylene vinyl acetate
EVOH	Ethylene vinyl alcohol
FAO	Food and agriculture organization
FAP	Food Additive Petition
FCN	Food Contact Notification
FDC	Food, drug and cosmetic
FDA	Food and drug administration
FSA	Food standards agency
G	Glucose
GRAS	Generally recognized as safe
GSTTC	Guideline for Screening Toxicity Testing of Chemicals
HSD	Honesty significant difference
IU	International unit
LLDPE	Linear low density polyethylene
MHW	Ministry of health and welfare
MD	Machine direction

NAS	National Academy of Sciences
OM	Overall migration
OS	Oxygen scavenger
TGA	Thermo gravimetric analyzer
PCR	Post consumer recycled
PET	Polyethylene terephthalate
PG	Propyl gallate
RARs	Retinoic acid receptors
RDA	Recommended Daily Amount
RE	Retinal Equivalents
RH	Relative humidity
RSM	Response surface methodology
SEM-EDS	Scanning electronic microscopy for energy-dispersive spectrometry
STP	Standard temperature and pressure
TNO	Netherlands Organization for Applied Scientific Research
TPP	Tetraphenyl prophine
TSCA	Toxic substances control act
XRF	X-ray fluorescence

Symbols

*	Represents an exited state of the species
c	Core layer of a film
Co	Oxygen uptake capacity (18 ccO_2/g)
Cst	Retinol concentration of standard solution (mg/100ml)
Csa	Retinol concentration of sample solution (g/100ml)
D	Density of the middle layer.
Di	New density of the blend with LLDPE or HDPE.
Ea	Activation energy (cal/mol)
$Fe(OAc)_2$	Iron compound mixed with ferric oxide
h	Interior height of the headspace in the package
i	Inner layer of a film
HAc	Acetic acid
HDDi	Density of HDPE
ΔH_{f1}	Heat of fusion of the sample (OS1)
ΔH_{f2}	Heat of fusion of the sample (OS2)
ΔH_{f^*}	Heat of fusion of 100% crystalline LLDPE (286.2 J/g)
Ka	Arrhenius equation constant
LaB_6	Lanthium hexaboride

LLDi	Density of LLDPE, and OS2Di was the density of OS2
M	Needed weight of oxygen scavenger material (M = 0.061 g)
Mi	Weight of the blend of LLDPE or HDPE with the oxygen scavenger
o	Outer layer of a film
$[O_2]$	Initial O_2 concentration in package (= 21% if air)
OS1	Oxygen scavenger 1
OS2	Oxygen scavenger 2
OS1Di	Density of OS1
OSl	Sachet had the form of a plastic cup
OS_L	Sachet laminated with paper and plastic
R	Universal gas constant (1.9872 cal/mol, K)
R^2	Regression coefficient of linear regression analysis
Rs	Response area for the sample (area unit: AU)
RH	Relative Humidity
S	Total interior surface of the package
Sh	Interior surface area of the headspace in the package
T	Absolute temperature (K)
Tg	Glass transition temperature
Tm	Melting temperature

Tmi	Desirable film thickness of the middle layer
Va	Air volume of the headspace
Vo	Volume of oxygen present in the headspace of the package

I. INTRODUCTION

1.1. Advances in cosmeceuticals

The term "cosmeceuticals" is a composite word of "cosmetic" and "pharmaceutical," and it was introduced by Albert Kligman 20 years ago at a meeting of the Society of Cosmetic Chemists, who defined it as topical formulations which lie between cosmetics and drugs. Some were closer to drugs, such as the alpha-hydroxy acids – designed to exfoliate the outer, loose stratum corneum, a structural effect – whereas others were closer to cosmetics, like rouge – designed to give color, a purely decorative effect (Kligman, 2005). The term "cosmeceuticals" has provoked discussions among scientists, the industry, and regulating authorities, because the introduction of cosmeceuticals enabled more precise classification of a product with an activity that is intended to treat or prevent a skin condition. New insights about the function of skin, as well as the development of new products for skin care, made it necessary to question or redefine the definitions of cosmetics and drugs, since the term is regarded as a subclass within the domain of cosmetics or drugs (Vermer, 2005).

However, according to the Food, Drug, and Cosmetic (FDC) Act, a drug is defined as an article intended to use in the diagnosis, mitigation, treatment, or prevention of disease or intended for affect the structure or any function of the body. On the contrary, a cosmetic is defined as an article intended to be rubbed, poured, sprinkled, or sprayed on, introduced into, or otherwise applied to the human body or any part thereof for cleansing, beautifying, promoting attractiveness, or altering the appearance without affecting structure or function, in 21 USC. As a result, the U.S. Food and Drug Administration (FDA), in accordance with the Food, Drug, and Cosmetic Act, does not recognize the term "cosmeceuticals" (FDA, 2000).

To avoid inquiry and punitive action by the United States Federal Trade Commission, cosmeceuticals are not intended to be regulated as drugs by the FDA are carefully labeled to avoid making statements which would indicate that the product has drug properties. Any such claims made regarding the product must be substantiated by scientific evidence as being truthful. It is to the financial benefit of the cosmeceuticals manufacturer that their products are not regulated by the FDA as drugs, because the regulation of a product as a drug requires many elaborate and costly procedures; therefore, the manufacturer of a product with pharmaceutical activity would prefer to have the product registered as a cosmetic (Elsner and Maibach, 2005).

The term cosmeceuticals is now commonly used to describe cosmetic products that are claimed, primarily by those within the cosmetic industry, to have drug-like benefits, because they contain active ingredients such as vitamins, herbs, enzymes, and antioxidants (Choi, et al., 2006; Schwartz, et al., 2008). Even if the term "cosmeceuticals" has no meaning under FDA regulations, the demands for these products have increased with the consequence that the market is expanding rapidly; the U.S. cosmeceuticals market will surpass $17 billion by 2010 from $7 billion in 2005; skin care, such as anti-aging creams and wrinkle remedies, is the largest segment (Granato, 2007). The global skin care market was valued at $50 billion and annual growth of 7 percent was expected between 2005 and 2009, making skin care the second-fastest growing cosmetics category, behind sun care products (MarketWikis, 2007).

New cosmeceutical ingredients which are derived from products with scientifically founded benefits in human health and its maintenance, such as vitamin A (retinol and all-*trans* retinoic acid named as tretinoin), vitamin C, alpha-hydroxy acids (AHAs), hydrolyzed proteins (from corn, soy, etc.) and polysaccharides (hyaluronic acid

and beta-glucans), are very remarkable additives (Applegate, 2002). Vitamins and their derivatives are often found in skincare products. Vitamins C and E have antioxidant properties. There is some research on the use of topical antioxidants for skin health. Topical application of vitamins C and E has shown significant photo protection against UV damage, possibly by scavenging reactive oxygen species (Eberlein-Konig, 2005). Various B vitamins also find their way into creams, including niacinamide (B3), which is said to increase the rate of exfoliation and barrier repair, and panthenol (pro-vitamin B5) which helps the skin retain its natural moisture. But the big one from an anti-wrinkle perspective is vitamin A (retinol) and its derivatives. Retinoic acid or tretinoin, which is the alternative name for *all-trans* retinoic acid (ATRA), is the strongest prescription, and the only product indicated for treating photo-damaged skin. The next strongest and common ingredient in skin cream is retinol itself and also pro-retinol, which are both involved in the growth and maturation of cells (Houlton, 2004).

1.2. Introduction to retinol

1.2.1. Definition and properties

Retinol was discovered by Elmer McCollum and Marguerite Davis who identified a fat-soluble nutrient in butterfat and cod liver oil in 1913. It was confirmed by Thomas Osborne and Lafayette Mendel, biochemists at Yale University, in 1913, as a fat-soluble nutrient in butterfat (Semba, 1999). Vitamin A was first synthesized by David Adriaan van Dorp and Jozef Ferdinand Arens in 1947.

Retinol, the parent vitamin A compound, has the molecular formula of $C_{20}H_{30}O$ and a molecular weight of 286.456 g/mol. As an animal form of vitamin A, it is a fat-soluble vitamin and has an important role in vision and bone growth. It belongs to the family of chemical ingredients known as retinoid. Figure 1 shows active retinoid metabolites (Chebigen, 2007). Retinol is ingested in precursor forms. One form is of animal origin, such as liver and eggs, which contain retinyl esters. The other form is acquired from plants. Particular green plants such as grass, clover, spinach and carrots are rich in pro-vitamin A carotenoids. Retinyl esters are converted into retinol through hydrolysis. Decomposition of pro-vitamin A carotenoids, the most well-known being beta-carotene, results in producing retinal. Retinal, known as retinaldehyde, can be reversibly reduced to produce retinol or it can be irreversibly chemically oxidized to produce retinoic acid. The best described active retinoid metabolites are 11-*cis*-retinal and the all-trans and 9-*cis*-isomers of retinoic acid (Ball, 2006).

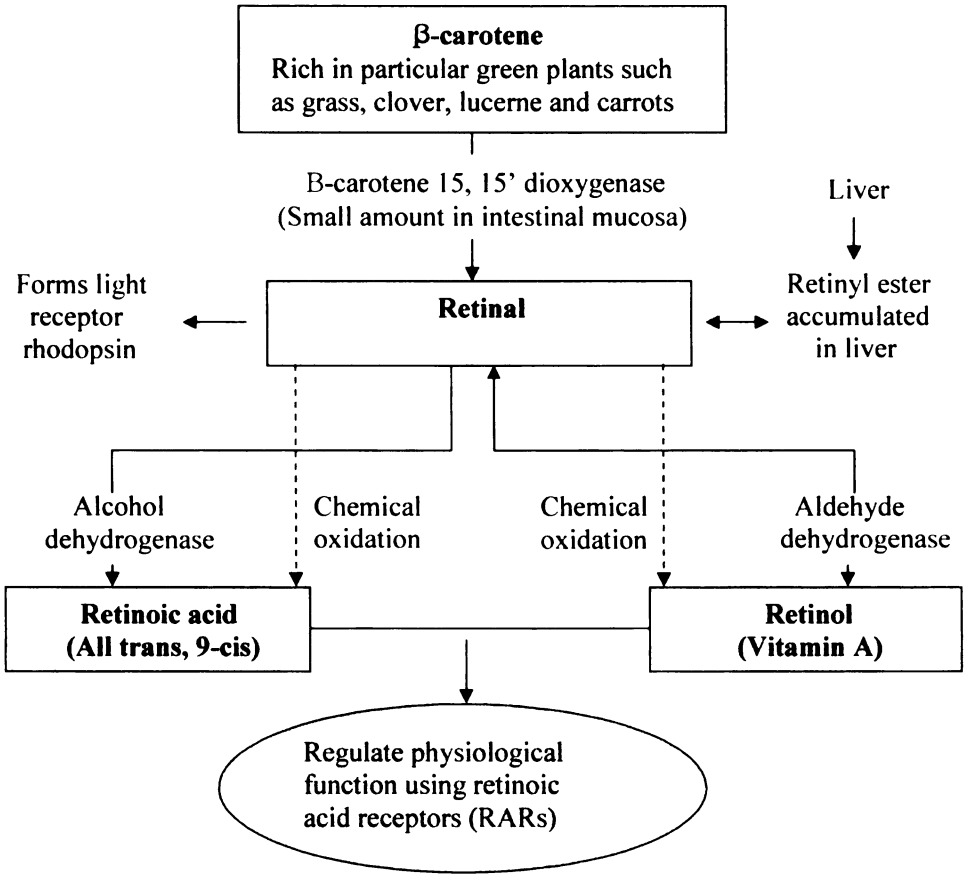
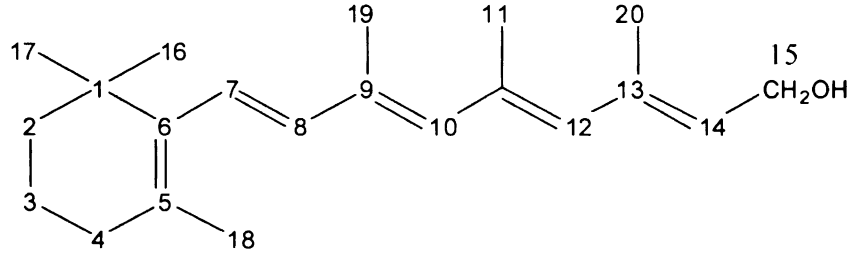


Figure 1. Metabolization mechanism of the retinol group
(Source: Chebigen, 2007)

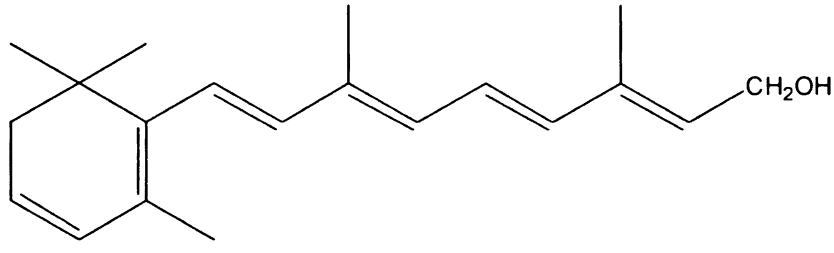
Many kinds of geometric isomers of retinol, retinal and retinoic acid are possible as a result of either a *trans* or *cis* configuration of four of the five double bonds found in the polyene chain. A polyene is a poly-unsaturated organic compound that contains one or more sequences of alternating double and single carbon-carbon bonds. These double carbon-carbon bonds interact in a process known as conjugation, which results in an overall lower energy state of the molecule. The *cis* isomers are less stable and can readily convert to the all-*trans* configuration. Nevertheless, some *cis* isomers are found naturally and carry out essential functions. For example, the 11-*cis*-retinal isomer is a chromophore

of the vertebrate photoreceptor molecule named rhodopsin. The process of vision relies on the light-induced isomerization of the chromophore from 11-*cis* to all-*trans*, resulting in a change of the conformation and activation of the photoreceptor molecule. Figure 2 shows the structures of retinoids found in foods and fish-liver oils (Ball, 2006).

(a) all-trans-retinol (Vitamin A1)



(b) all-trans-3-dehydroretinol



(c) 13-cis-retinol

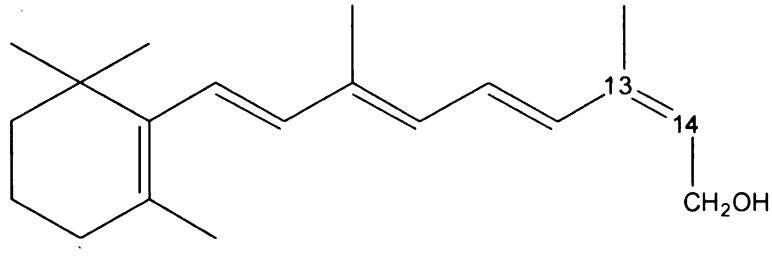
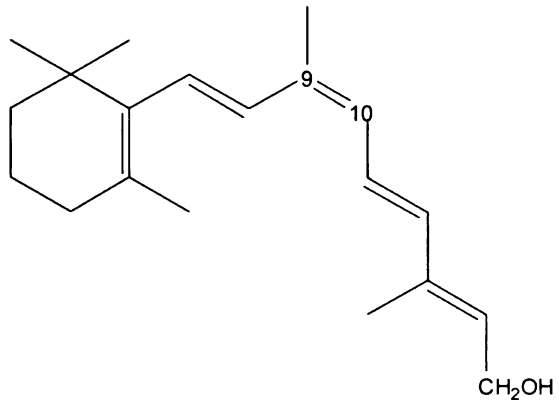


Figure 2. Structure of retinoids

(d) 9-cis-retinol



(e) 9,13-dis-cis-retinol

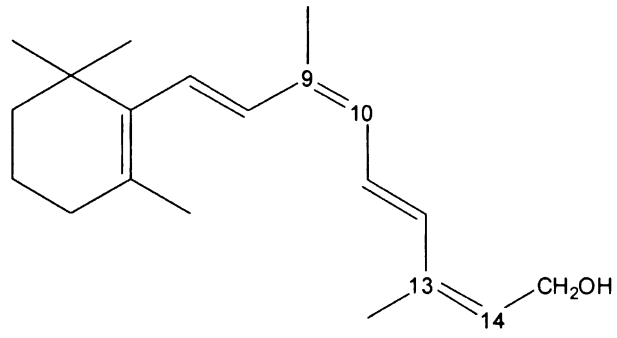


Figure 2. Structure of retinoids *(continued)*

1.2.2. Applications

All kinds of retinoids in vitamin A are used in cosmetic and medical applications applied to the skin. Tretinoin, under the alternative name of *all-trans* retinoic acid (ATRA), is used in the treatment of acne and keratosis in a topical cream, and is used as chemotherapy for a subtype of leukemia, because the cells of leukemia are sensitive to agonists of the retinoic acid receptors (RARs). An isotretinoin is also used for severe or recalcitrant acne.

In cosmetics, vitamin A derivatives are used as anti-aging chemicals, which are absorbed through the skin and increase the rate of skin turnover, and give an increase in collagen giving a more youthful appearance. Although topical vitamin A is not very effective as a skin care ingredient, other members of retinoid family such as retinol and retinoic acid have long been used for the treatment of acne and wrinkles. In skin care products, retinol is the first antioxidant to be widely used in nonprescription functional cosmetics such as wrinkle creams. Antioxidants are substances that neutralize free radicals - unstable molecules that break down skin cells and cause wrinkles.

According to a new study from the University of Michigan Health System, lotions containing retinol improve the appearance of skin that has become wrinkled through the normal aging process, not just which has been damaged by exposure to sunlight. During the study, led by doctors at the U. of M. Medical School, 0.4% retinol was applied to 36 subjects with a mean age of 87, up to three times per week. After 24 weeks, the improvement of retinol-treated skin was dramatic, and clearly visible to the naked eye (Kafi et al., 2007).

1.2.3. Nutrition and dietary intake

Vitamin A is protected from being chemically changed by vitamin E in the intestine. Vitamin A is fat-soluble and can be stored in the body. Most of the vitamin A after eating is accumulated as retinyl ester in the liver, and when retinol is needed in other tissues or cells, it is de-esterified and released into the blood as the alcohol.

When referring to dietary allowances or nutritional science, retinol is usually measured in international units (IU), which refers to biological activity and therefore is unique to each individual compound. One IU of retinol is equivalent to approximately 0.3 micrograms (300 nanograms). Amounts of vitamin A are measured in Retinal Equivalents (RE), and 1 RE is equivalent to 0.001 mg of retinal, or 0.006 mg of beta-carotene, or 3.3 IU of vitamin A, according to the Food and Agriculture Organization (FAO) of the United Nations (FAO, 1967). The Dietary Reference Intake (DRI) Recommended Daily Amount (RDA) for vitamin A for a 25-year old male is 900 micrograms (3,000 IU) per day, and 700 micrograms (2,333 IU) per day for adult females. The RDA upper limit for both adult males and females is 3,000 micrograms (10,000 IU) per day, according to the National Academy of Sciences (NAS) in the U.S. (NAS, 2004). Synthetic forms prescribed for therapeutic purposes such as certain skin disorders and multi-vitamin supplements are at levels up to 2,400 micrograms (approximately 8,000 IU) per daily dose, by the Expert Group on Vitamins and Minerals (EGVM) of the Food Standards Agency (FSA) in the U.K. (EGVM, 2003).

1.3. Major factor in packaging design

Retinol has attracted considerable attention lately as a new functional ingredient that plays an important role in epidermal cells to maintain their original capacity. However, retinol is a group of fat-soluble compounds that has an unstable structure consisting of a β-ionone ring, a conjugated isoprenoid side chain and a polar terminal group (-OH). Therefore, it is readily oxidized or isomerized to altered compounds, especially in the presence of oxidants including air, and influences such as light and heat. It is labile toward active components such as silica, strong acids and solvents that have dissolved oxygen or peroxides (Ball, 2006; EGVM, 2003; Barua and Harold, 1998).

Retinol is easily decomposed by atmospheric oxygen, resulting in an almost complete loss of biological activity. Even though retinyl esters are somewhat more stable than retinol, they are also readily oxidized. Retinol is extremely sensitive to acids, which can cause rearrangement of the double bonds and dehydration. Solutions of all-*trans*-retinol or retinyl palmitate in hexane undergo slow isomerization to the lower potency *cis* isomers when exposed to white light, but retinyl palmitate is stable in chlorinated solvents when it is stored in the dark. Vitamin A is easily decomposed by irradiation and forms inactive structures that cause a yellowish color. While the carotenoids are stable within natural plant cells, they are apt to be transformed by *trans* to *cis* isomerization and degradation by heat, light, oxygen, acids, and silica (Ball, 2006).

Therefore, the most important factor in developing commercial products and packaging to contain vitamin A such as retinoids and provitamin A carotenoids, is how to prevent the decomposition from heat, light, oxygen and other active components (Barua and Harold, 1998). A great deal of care is required not only in product processing, but also in all the shelf-life including storage, transportation and distribution channels.

This kind of product can be readily oxidized and photo-degraded by the residual oxygen in the headspace and the transmitted light in or through a conventional plastic package. In the cosmeceuticals industry, especially, solving this kind of problem is an increasing issue. For this reason, the manufacturers will have paid an extra charge for initially putting an excess of the functional ingredients such as retinol into the product. Therefore, if certain packaging could protect vitamin A against degradation from light and oxygen, manufacturers are quite willing to pay for an effort to develop the packaging.

1.4. References

Applegate, D.R. and Julie A. Reynolds, "Rejuvenation of Aging and Photodamaged Skin Utilizing Fibroblast Conditioned Media," in New York SCC '01, 2001 Speaker of the Year Award, Sep. 24, 2002. http://www.nyscc.org/news/archive/rech0902.htm

Ball G.F.M., *Vitamins in Food: Analysis, Bioavailability, and Stability*, CRC Press, Taylor & Francis Group, Boca Raton, FL, pp. 39-51, 2006.

Barua, A.B. and C.F. Harold, "Properties of retinols," *Molecular Biotechnology*, 10: 167-182, 1998. http://www.springerlink.com/content/b234wu0t1h607182/

Chebigen, "Retinol and retinol derivatives," undated. http://www.chebigen.com/english/business_1.htm, (accessed Nov. 23, 2007)

Eberlein-Konig, B., "Relevance of vitamins C and E in cutaneous photoprotection," *Journal of Cosmetic Dermatology*, 4(1): 4-9, Jan. 2005.

EGVM (Expert Group on Vitamins and Minerals), "Safe Upper Levels for Vitamins and Minerals," Food Standards Agency (FSA), UK, PP. 110-126, May 2003. http://www.food.gov.uk/multimedia/pdfs/evm_a.pdf

FAO (Food and Agriculture Organization of the United Nations), "Factors for vitamin A conversion," FAO Report Ser. No. 41, 1967. http://www.fao.org/docrep/003/X6877E/X6877E22.htm, (accessed DEC. 27, 2007)

FDA (U.S. Food and Drug Administration), "Cosmeceutical," Feb. 24, 2000. http://www.cfsan.fda.gov/~dms/cos-217.html

Granato, H., "Cosmeceuticals: At the Intersection of Nutrition and Beauty," *Natural Products Insider*, June. 4, 2007. http://www.naturalproductsinsider.com/articles/472/75h318454835771.html

Houlton, S., "Natural skin science," Apr. 19, 2004. http://www.users.globalnet.co.uk/~sarahx/articles/cicosmeceuticals.htm

Kafi, R., Heh Shin Kwak, E. Wwndy, Schumacher, Soyun Cho, Valerie N. Hanft, Ted A. Hamilton, Anya L. King, Jacqueline D. Neal, James Varani, Gary J. Fisher, John J. Voorhees, Sewon Kang, "Improvement of Nationally Aged Skin With Vitamin A (Retinol)," *Arch Dermatol*, 143: 606-612, 2007.

MarketWikis, "Anti-Aging Market Research," Nov. 25, 2007. http://www.researchbuy.com/,arketwikis/Anti-Aging_Market_Resarch

NAS (National Academy of Sciences), "Dietary Reference Intakes (DRIs): Recommended Intakes for Individuals, Vitamins", 2004. http://www.iom.edu/Object.File/Master/21/372/0.pdf

Semba R.D., "Vitamin A as "Anti-Infective" Therapy, 1920-1940," *Journal of Nutrition*, 129: 783-791, 1999.

2. LITERATURE REVIEW

2.1. Active packaging systems

2.1.1. Definition of active packaging

In recent years, new packaging systems have been developed as a response to the continuing increase in consumer demands for fresh, tasty and convenient food products with extended shelf-life. Furthermore, changes in retail systems such as centralization of activity and globalization of markets result in longer distribution distances, required innovative packaging concepts that extend shelf-life while maintaining the safety and quality of the packaged product, because traditional systems were not reaching their goal with regard to further prolongation of the shelf-life of packaged products (De Kruijf et al., 2002). As a consequence, various new packaging technologies or systems were introduced, named active, smart, clever, or intelligent packaging. The first use of the term 'active packaging' was at the Icelandic conference on nutritional impact of food processing in 1987 by Professor Labuza from the University of Minnesota (Labuza and Breene, 1989), and the term may be defined as packaging which performs some desired function other than merely providing a barrier to the external environment (Hotchkiss, 1995). More recently, this term was more clearly defined by Robertson as follows: "Active packaging is that packaging in which subsidiary constituents have been deliberately included in either the packaging material or the package headspace to enhance the performance of the package system" (Robertson, 2006).

But, these terms are undefined and often misused in the literature. For this reason, twelve partners from research and industry organized to define active and intelligent packaging systems in 1999 under the name of 'Actipak project' in Europe (TNO, 2002).

This resulted in the adoption of a new Framework Regulation (1935/2004/EC) in which the use of active and intelligent packaging systems is now included (De Jong et al., 2005). According to the definitions of the Actipak project, active packaging changes the condition of the packed food to extend shelf-life or improve safety or sensory properties, while maintaining the quality of the packed food (Rijk et al., 2002).

In the definition of active packaging, foods undergo various processes that may affect the shelf-life of packed products: physiological processes such as respiration of fresh fruit or vegetables, chemical or physical processes such as lipid oxidation or staling of bread, and other processes such as spoilage by micro-organisms or insects. Through the application of appropriate active packaging systems, the food condition can be improved in various ways, and the shelf life of the packaged products will be extended by reduced food deterioration (De Kruijf et al., 2002).

2.1.2. Active packaging technologies

For preservation and improving quality and safety of products, active packaging techniques can be classified as three types of systems: absorbing or scavenging systems [Table 1], releasing systems, and other systems (Ahvenainen, 2003). A scavenging system is one that removes or absorbs undesired substances such as oxygen, carbon dioxide, ethylene, humidity or other compounds such as off-flavors or lactose. A releasing system emits specific compounds, such as carbon dioxide, antioxidants and antimicrobial preservatives, into the headspace of the package or the packaged food.

Other systems may have various tasks, such as self-heating and cooling packages, microwave susceptors, and widgets that produce foams in beer cans (Robertson, 2006; Bohrer and Brown, 2001).

Table 1. Examples of sachet, label and film type absorbing (scavenger) active packaging systems for preservation and shelf-life extension of foods or improving their quality and usability for consumers. Oxygen, carbon dioxide, ethylene and humidity absorbers have the most significant commercial use; lactose and cholesterol removers are not yet in use. (Source: Ahvenainen, 2003)

Packaging type	Examples of working principle/ mechanism/reagents	Purpose	Examples of possible applications
Oxygen absorber (sachets, labels, films, corks)	Ferro-compounds, ascorbic acid, metal salts, glucose oxidases, alcohol oxidase	Reduction/prevention of mold, yeast and aerobic bacteria growth Prevention of oxidation of fats, oils, vitamins, colors Prevention of damage by worms, insects and insect eggs	Cheese, meat products, ready-to-eat products, bakery products, coffee, tea, nuts, milk powder
Carbon dioxide absorbers (sachets)	Calcium hydroxide and sodium hydroxide or potassium hydroxide Calcium oxide and silica gel	Removing of carbon dioxide formed during storage in order to prevent bursting of a package	Roasted coffee, beef jerky, dehydrated poultry products
Ethylene absorbers (sachets, films)	Aluminum oxide and potassium permanaganate (sachets) Activated carbon + metal catalyst (sachet) Zeolite (films) Clay (films) Oya stone (films)	Prevention of too fast ripening and softening	Fruits such as apples, apricots, bananas, mangos, cucumbers, tomatoes, avocados Vegetables such as carrots, potatoes and brussels sprouts
Humidity absorbers (drip-absorbent sheets, films, sachets)	Polyacrylates (sheets) propylene glycol (film) Silica gel (sachet)	Control of excess moisture in packed food Reduction of water activity on the surface	Meat, fish, poultry, bakery products or fruit and vegetables

Table 1. (*continued*)

Packaging type	Examples of working principle/ mechanism/reagents	Purpose	Examples of possible applications
	Clays (sachet)	of food in order to prevent the growth of mold, yeast, and spoilage bacteria	
Absorbers of off flavors, amines and aldehydes (films, sachets)	Cellulose acetate film containing naringinase enzyme Ferrous salt and citric or ascorbic acid (sachet) Specially treated polymers	Reduction of bitterness in grapefruit juice Improving the flavor of fish and oil-containing food	Fruit juices Fish Oil-containing foods such as potato chip, biscuits and cereal products Beer
UV-light absorbers	Polyolefins like polyethylene and polypropylene doped with a UV absorbent agent UV stabilizer in polyester bottles	Restricting light-induced oxidation	Light-sensitive foods such as ham Drinks
Lactose remover	Immobilized lactase in the packaging material	Milk products for people with lactose intolerance	Milk and other dairy products
Cholesterol remover	Immobilized cholesterol reductase in the packaging material	Improving the healthiness of milk products	Milk and other dairy products

Absorbers and releasers can be sachet, label or film types. While sachets are placed freely on products in a package, labels are attached to the inside of a package and generally do not directly contact the food unless the package is turned over. The film type

is often used in cases where the ingredients impair the function of the system or may cause migration problems.

2.1.3. Current use and future trends

In the USA, Japan and Australia, active packaging systems are already being successfully applied to prolong the shelf-life of packaged products. However, there are only a few commercially significant systems on the market. Oxygen absorbers added separately as small sachets in the package headspace or attached as labels into the lid probably have the most commercial application in active food packaging at present. Other commercially significant active technologies, such as ethanol emitters or ethylene absorbers, are less used than oxygen absorbers. In Europe, only a few of these systems have been developed and are being applied due to the strict European regulations for food contact materials that have not kept up entirely with technological innovations and currently prohibit the application of many of these systems.

However, the use of proper packaging materials and methods to minimize food losses and provide safe and wholesome food products has always been the focus of packaging. In addition, consumer demands for better quality, fresh-like, and convenient food products have intensified during the last decades. The future trend in active packaging is to use scavenging or releasing compounds incorporated in the packaging film or in an adhesive label to eliminate the requirement for separate objects in the package, because sachets suffer from inadequate consumer acceptance due to fears of ingestion by children and accidental consumption with the package contents. These invisible active scavengers or emitters will be commercialized widely in the near future (Ahvenainen, 2003; Ozdemir and Floros, 2004).

The market for active packaging films was a modest $50 million worldwide in 2003, and was expected to grow rapidly (Ozdemir and Floros, 2004). According to a new Freedonia Group study, the demand for active packaging will reach $975 million by 2011 in the US, driven by 11 percent annual growth in innovation and the need to improve shelf life and safety. Food applications are expected to rise 12 percent a year to $435 million in 2011, driven by the demand for longer shelf life for processed and packaged foods. The market for organic products and removal of trans-fats from processed food will also boost oxygen scavenging packaging. The beverage and beer market for polyethylene terephthalate (PET) bottles incorporating oxygen scavengers is expected to reach $395 million in 2011, with a 15 percent annual increase (Reynolds, 2007). Gas scavengers were the most used products in the active packaging segment in 2006, representing over 50 percent of demand. In the pharmaceutical market, compliance monitoring devices and active reminder products are expected to increase. The demand for moisture control active packaging is also expected to expand due to pharmaceutical shipment growth and the increasing number of drugs with high moisture sensitivity (Bharat, 2007).

2.2. Oxygen scavenger systems

High levels of oxygen present in packed products may facilitate microbial and insect growth, and accelerate off-flavor development by rancidity as a result of lipid oxidation; color changes by discoloration of plant pigments such as chlorophyll and carotenoids; and nutrient losses by oxidation of vitamin E, β-carotene (pro-vitamin A), and ascorbic acid (vitamin C). Thereby, it may cause significant reduction in the shelf-life of products. The oxygen present may derive from oxygen permeability of the packaging material, air enclosed in the food and packaging material, or a small amount of leakage due to poor sealing (Smith et al. 1986). Therefore, the reduction of the oxygen level in packed product has an important role in limiting this deterioration and spoilage of foodstuffs. Oxygen scavenging systems provide an alternative to vacuum and gas flushing packaging and extend the shelf life, because they can provide removal of oxygen in packed products using techniques variously called absorption, interception, or scavenging. In many cases, this is the most important active packaging objective.

2.2.1. Definitions

The terms antioxidants, interceptors, absorbers, and scavengers have been used to describe the materials employed in the process of removing oxygen or preventing it from entering the in-package environment of food products subject to undesirable oxidative reactions. These definitions do not have clear boundaries, and are often used in overlapping ways (Brody et al., 2001).

2.2.1.1. Antioxidants

Antioxidants generally are compounds that react with lipid or peroxide radicals, and that are themselves oxidized to generate what are generally nontoxic compounds.

Antioxidants are commonly fat soluble components incorporated into fatty foods to preferentially react with intermediate oxidation products. These lipid antioxidants include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and propyl gallate (PG), and are often blended with lipids to retard their oxidation. The BHA/BHT compounds are also often incorporated into polyolefin packaging films to retard the oxidation of the plastic materials themselves. Recently, antioxidants less volatile than BHT for HDPE and LLDPE, such as polyphenols, have been used in combination with phosphates. Alpha tocopherol (vitamin E) is also used as an antioxidant for polyolefins (Selke et al., 2004).

2.2.1.2. Oxygen interceptors

Interceptors are compounds that prevent oxygen from reaching the food product by themselves being oxidized before the oxygen reacts with the food. The word interceptor has often been used as a descriptor on food labels to avoid statements about antioxidants that may have the image to consumers of undesirable chemicals.

2.2.1.3. Oxygen absorbers

Technically, absorbers remove oxygen by physically trapping the oxygen and not through chemical reaction. However, there are seldom useful materials to remove oxygen without any chemical oxidation. Therefore, this word is generally used to describe the systems that remove oxygen to delay or prevent oxidation of foodstuffs. Oxygen absorbers can be applied as sachets that are filled with oxygen absorbing components such as iron particles and salt. They are inserted into the package or adhere to the inner wall or lid of the package.

2.2.1.4. Oxygen scavengers

The oxygen scavenger has been applied to materials incorporated into package structures that chemically combine with, and thus effectively remove, oxygen from the inner package environment. In addition, scavengers may remove oxygen from the food product itself through diffusion resulting from differential partial pressure actions [Figure 3].

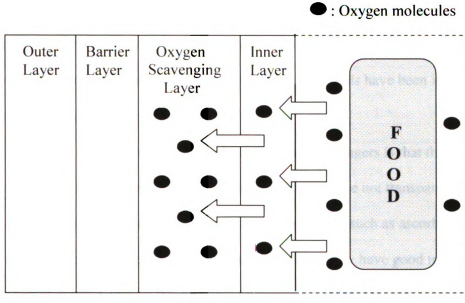


Figure 3. Structure of a typical oxygen scavenging multi-layer film (Source: Ozdemir and Floros, 2004)

2.2.2. Oxygen scavenging/absorbing technologies

As mentioned in section 2.2.1, oxygen scavenging/absorbing technologies can be applied as sachets containing oxygen absorbing components, which are inserted into the package or are tagged onto the inner wall in the package as labels or card types. They can also be incorporated into the closure liners or containers through compounding with plastic materials or fixation of oxidizing enzymes in the packaging material.

Even though they have higher oxygen absorbing capacity than other oxygen scavenging systems, these sachet and label types have disadvantages in some commercial practices. The first is that they are not appropriate for liquid products because the direct contact of the products with the sachet usually causes spillage of the sachet contents. Secondly, the sachets may accidentally be consumed with the food or may be ingested by children. Thirdly, they are inappropriate in tube type containers because of inserting or tagging problems. In addition, although sachets can be considered as secondary packaging, these practices can increase packaging costs by requiring the operation of an additional sachet tagging and inspection line. For these reasons, oxygen scavengers of polymeric type that are incorporated into packaging materials have been introduced as an alternative to the sachet type.

Another problem in use of iron-based oxygen scavengers is that they generally cannot pass the metal detectors on the packaging line and are not transparent. Consequently, organic based oxygen scavenging materials, such as ascorbic acid or enzyme based materials, have been introduced, because they have good transparency and allow use of metal detection (Hurme and Ahvenainen, 1996). Despite these advantages, their low oxygen scavenging capacity and high cost are innate problems in these systems.

Generally, oxygen scavenging technologies are classified as enzymatic or chemical systems, and can utilize one or more of the following mechanisms: iron powder oxidation, ascorbic acid oxidation, sulfite oxidation, photosensitive dye oxidation, ferrous salts, unsaturated fatty acids and enzymatic oxidation such as glucose oxidase, and combinations of these (Day, 2000, 2003: Brody, 2001). Table 2 provides a list of some manufacturers and trade names of oxygen scavengers. The major products are iron based

sachet types, and some of these are useful to make film or other container types through incorporating oxygen scavengers into polymeric materials. Especially, Oxyguard® of Toyo Seikan and Shelf Plus® of Ciba Specialty Chemical have been commercialized as films or trays. Recently, organic oxygen scavengers were commercialized with development of polyethylene terephthalate (PET) bottles, bottle caps and crowns for beer and other beverages (Vermeiren et al., 2003).

Table 2. Selected commercial oxygen scavenger systems.
(Source: Vermeiren et al., 2003; Day, 2003)

Manufacturer	Country	Trade Name	Scavenger mechanism	Packaging Form
Mistubishi Gas Chemical	Japan	Ageless	iron based	sachets, labels,
Toppan Printing	Japan	Freshilizer	iron based	sachets
Toagosei Chem. Industry	Japan	Vitalon	iron based	sachets
Nippon Soda	Japan	Seagul	iron based	sachets
Toyo Pulp	Japan	Tamotsu	catechol	sachets
Toyo Seikan Kaisha	Japan	Oxyguard	iron based	plastic tray, film
Multisorb Technologies	USA	FreshMax FreshPax	iron based iron based	labels sachets
Dessicare	USA	O-Buster	iron based	sachets
Amoco Chemicals	USA	Amosorb	unknown	plastic film
Chevron Chemicals	USA	N/A	benzyl acrylate	plastic film
W.R. Grace and Co.	USA	PureSeal	ascorbate/ metallic salt	bottle crowns
		Darex	ascorbate/	bottle crowns

Table 2. *(continued)*

Manufacturer	Country	Trade Name	Scavenger mechanism	Packaging Form
			sulphite	bottles
Cryovac Sealed Air	USA	OS1000	light activated	plastic film
Ciba Speciality Chemical	Switzerland	Shelfplus	iron based	plastic tray, film
CSIRO/Southcorp Packaging	Australia	$ZERO_2$	photosensitive dye/ organic	plastic film
CMB Technologies	France	Oxbar	cobalt catalyst/ nylon polymer	plastic bottles
Standa Industries	France	ATCO Oxycap	iron based iron based	sachets, labels bottle crowns
EMCO Packaging System	UK	ATCO	iron based	labels
Johnson Matthey Plc	UK	N/A	platinum group metal catalyst	labels
Alcoa CSI Europe	UK	O_2 displacer system	unknown	bottle crowns
Bioka	Finland	Bioka	enzyme based	sachets

2.2.2.1. Iron based oxygen scavengers

Among the several active components that absorb oxygen, iron based materials are most commonly used. Iron power can reduce the oxygen concentration in the headspace to less than 0.01%, which is much lower than the typical 0.3 to 3.0% residual oxygen levels achievable by using modified atmosphere packaging such as vacuum or gas flushing technologies (Day, 2000).

Any oxygen within or entering into the package oxidizes the iron to the ferric state in the present of moisture drawn from the product or process. This is the basic mechanism of corrosion or rusting. The reaction mechanism has the following steps (Vermeiren et al., 2003):

$$4\ Fe \rightarrow 4\ Fe^{+2} + 8\ e^{-} \quad (2.1)$$

$$2\ O_2 + 4\ H_2O + 8\ e^{-} \rightarrow 8\ (OH)^{-} \quad (2.2)$$

$$4\ Fe^{+2} + 8\ (OH)^{-} \rightarrow 4\ Fe(OH)_2 \quad (2.3)$$

$$4\ Fe(OH)_2 + O_2 + 2\ H_2O \rightarrow 4\ Fe(OH)_3 \quad (2.4)$$

$$4\ Fe(OH)_3 \rightarrow 2\ Fe_2O_3 + 6\ H_2O \quad (2.5)$$

The stoichiometry of the reaction allows calculation of the amount of oxygen that reacts with iron. One gram of iron reacts with 0.0136 mol of O_2, which is equal to approximately 330 cm^3 of oxygen (STP) (Labuza and Breene, 1989), but the efficiency can be reduced about half by particle agglomeration (Brody et al., 2001).

Several environmental conditions encountered by food packages affect the overall oxygen absorption (or scavenging) rate of powered iron. The most important factors include temperature and relative humidity. The effect of temperature on reaction kinetics can be expressed by the Arrhenius equation:

$$k = k_A \exp\left(-\frac{E_A}{RT}\right) \quad (2.6)$$

where k is the reaction rate at a given temperature (T), k_A is the Arrhenius equation constant, E_A is the activation energy (cal/mol), R is the universal gas constant (1.9872 cal/mol K), and T is absolute temperature (K). If the reaction rates are determined at several temperatures, then k_A and E_A can be calculated.

Moisture is necessary for the process of oxygen absorption by iron (Equation 2.2), indicating that relative humidity is an important factor for the reaction. Commercial oxygen absorbing sachets used in foods are produced for use at different water activities (a_w). For an a_w greater than 0.85, powdered iron reacts at an acceptable rate for commercial applications. However, for an a_w below 0.85, an additive is needed to bring moisture into contact with the iron powder.

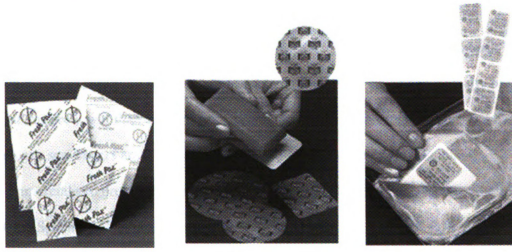
Another important factor during oxygen absorption by powdered iron is the presence of a catalyst. NaCl has been used as a catalyst (Klein and Knorr, 1990), because it allows the first two reactions (Equations 2.1 and 2.2) to occur more readily. Klein and Knorr (1990) reported that 2.0 g NaCl/100 g powdered iron gave optimum results for the maximum oxygen absorption rate. According to Farkas (1998), the oxygen absorption kinetics of powdered iron containing NaCl as a catalyst were optimized using response surface methodology (RSM) at 56 ℃, 78% RH and 0.8 % NaCl.

1) Sachet and pad (label and card) type

The first major commercial oxygen scavengers, under the trade name of Ageless®, were from Mitsubishi Gas Chemical Company in 1977. They introduced reduced iron salts into oxygen permeable sachets, which were placed in sealed gas barrier food packages. In-package oxygen absorber sachets are available commercially with the ability to consume 20 to 2,000 cc of oxygen, based on using packages with oxygen permeability no greater than 20 cc/m^2/day (Robertson, 2006).

After the advent of Ageless® (Japan), the sachet types of oxygen absorbing systems that have been used the most commonly are as follows: Freshpax® (Multisorb

Technologies, Inc., USA), ATCO® (Standa Industries, France), and Freshilizers series (Toppan Printing, Japan). Recently, integrated systems have been developed that include oxygen-scavenging labels or cards, such as the Freshmax® and Agless® series, which are inserted into the package or adhere to the inner wall or lid of the package as sachet, card and label types [Figure 4].



Sachet type Card type Label type

Figure 4. Types of oxygen absorbers

Now, these iron-based oxygen absorbers have the ability to reduce oxygen in many humidity conditions, including high, intermediate, or low moisture foods or pharmaceuticals. They can also work at refrigerated conditions. In particular, they have demonstrated the effectiveness of oxygen removal in various foodstuffs such as bakery, fish, pasta, meat, and beverage products such as beer, juice and wine (Gill and McGinnes 1995; Berenzon and Saguy 1998, Vermeiren et al., 1999).

The possible accidental ingestion of the sachet contents by the consumer has been suggested as a reason for their limited commercial success, particularly in North America and Europe. As a result, the largest sachet commercially available contains 7 g of ferrous

iron, which would amount to only 0.1 g/kg for a 70 kg person, or 160 times less than the lethal dose for adults. The product has been approved by the Japanese Ministry of Health and the United States Food and Drug Association (FDA), provided there is a warning label of "Do not eat" on the package (Brody et al., 2001).

2) Polymeric type

Recently, the incorporation of oxygen scavengers in packaging has been seen as a better way of resolving sachet related problems even if the speed and capacity of these systems are lower than those of sachets and labels. Low molecular weight iron based oxygen scavengers are dissolved or dispersed in plastic materials. The major commercialized products are as follows: Oxyguard® (Toyo Seikan, Japan), Shelf Plus® (Ciba Specialty Chemicals Corporation, Switzerland), and Ageless® OMAC (Mitsubishi Gas Chemical, Japan). Mitsubishi Gas Chemical launched a new oxygen scavenger in a sachet type (Ageless® FS), which no longer uses powdered ingredients. This new, slim type looks like the current sachet style; it contains an oxygen scavenging plastic sheet instead of powdered ingredients [Figure 5].

Ageless® FS is made of a sheet-like label that is mixed with fibrous material, ferrous iron powder, water, and an electrolyte and is formed by a process similar to paper making. Ageless® OMAC film is ideal for high A_w solid and liquid food, especially for retorted foods.

Shelf Plus® (tray) Ageless® OMAC (film) Ageless® FS (sheet)

Figure 5. Polymeric type oxygen scavenger (iron based)

Oxyguard® of Toyo Seikan can be used as a thermoformed tray, a laminated film, or a bottle closure liner, according to their patent (Koyama et al., 1993) [Figure 6]. The major developments are a heat formable oxygen absorbing resin and an oxygen scavenger. The resin is a blend of a polyolefin with a water absorbing resin such as a modified polyethylene oxide, a vinyl alcohol polymer, a sodium acrylate polymer, or an acrylic acid/vinyl alcohol copolymer with polyolefin resin. The oxygen scavenger can be mixed with accelerators such as hydroxides, carbonates, sulfites, halides of alkali metals, and alkaline earth metals. The particle size of reduced iron ranges from 0.1 to 100 μm. The smaller the particle size of iron, the bigger the oxygen scavenging capacity is. However, if the particle size is smaller than 1.0 μm, a special extrusion system is needed to prevent explosion due to heat generation during the mixing process. Oxidation promoters used are chlorides of alkali metals and/or alkaline earth metals such as NaCl or $CaCl_2$. The oxygen scavenger resin is mixed with 7 percent of powdered iron particles by weight, and the amount of oxidation promoter is 2 to 10 percent of the iron powder weight. Klein and

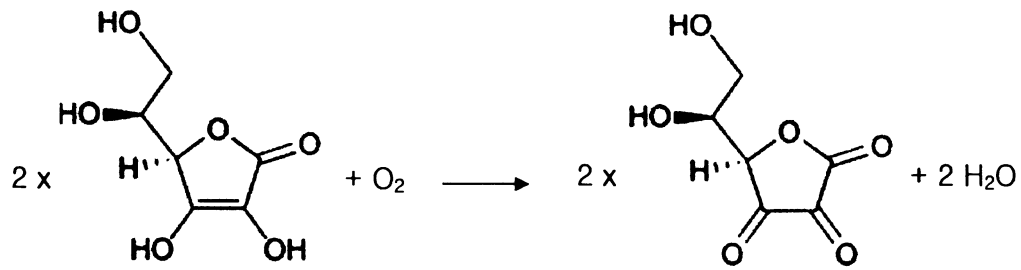
Knorr (1990) reported that 2.0 g NaCl/100 g powdered iron gave optimum results for the maximum oxygen absorption rate.

Figure 6. Oxyguard ® (tray)

The original technology of Shelf Plus® of Ciba Specialty Chemicals was developed from Amoco Chemicals. The composition has not been revealed, but it is an iron-based oxygen scavenger which is moisture activated. The O_2-2400 series is used for polyethylene carrier resin for blown film and the O_2-2500 series is intended for polypropylene carrier resin for retort packages. The oxygen uptake capacity of O_2-2400 is known to be 18 cc O_2/g by their test method and for O_2-2500 is 12 cc O_2/g. All contents were determined to be GRAS (generally recognized as safe) for use in multi-layer food packaging according to U.S. FDA regulations. The absorbent layer must be separated from the product by a sealant layer at least 12.5 μm (0.0005 inch) thick in plastic film structures, and 25 μm (0.001 inch) thick in multi-layer sheets. Use of these oxygen scavengers in multi-layer constructions is in compliance with the U.S. Federal Food, Drug, and Cosmetic Act and all applicable food-additive regulations (Brody et al., 2001).

2.2.2.2. Ascorbic acid oxygen scavenger

The next commercially important oxygen scavenger is ascorbic acid and its derivatives. The oxidation reaction mechanism of ascorbic acid, which has six carbon atoms ($C_6H_8O_6$), is shown in Figure 7. To convert it to dehydroascorbic acid ($C_6H_6O_6$), metal ions such as iron are needed as a catalyst.



Ascorbic Acid Dehydroascorbic Acid

Figure 7. Oxidation mechanism of ascorbic acid

This technology was developed by Toppan Printing in Japan and applied to packages for ground coffee and bread. The oxygen scavengers of Grace's Daraform®, which are ascorbic acid analogues have been used by incorporation into plastic bottle closure liners (UNCTAD/WTO, 1992). Darex® Container Products (now Grace Performance Chemicals, USA) developed a new organic oxygen scavenger named DarEval with Kuraray in Japan, which mixed ethylene vinyl alcohol (EVOH) with this material, and was designed for PET beer bottles (PET Planet Insider, 2000).

2.2.2.3. Sulfite oxygen scavengers

In the late 1950s, sulfite oxygen scavengers were developed by the Carnation Company, which used sulfite salt with copper sulfate as a catalyst for oxygen absorbing. In 1980, the Metal Box Company in the UK was granted a patent for an oxygen

scavenger in a wine bottle bung or cork using sodium metabisulfite plus sodium carbonate to release sulfur dioxide. The cork or bung was formed by an injection molding process in which sulfur dioxide, carbon dioxide, and water vapor were produced to fill voids within the EVA material. This residual SO_2 and water vapor trapped in the voids react with entering oxygen (Brody, 2001):

$$2\ SO_2 + O_2 + 2\ H_2O \rightarrow 2\ H_2SO_4 \qquad (2.7)$$

American National Can Company (now, Pechiney Plastics) developed multi-layer barrier plastic cans which incorporated potassium sulfite oxygen scavenger using a co-injection blow molding process. This oxygen scavenger can be readily triggered by the moist high temperature of the retorting process (Farrell and Tsai, 1987). Figure 8 shows commercialized products using plastic cans incorporating potassium sulfite oxygen scavenger.

Figure 8. Plastic cans incorporating potassium sulfite oxygen scavenger (Source: www.hormelfoods.com/brands/hormel/HormelMicrowaveCups.aspx)

2.2.2.4. Photosensitive dye oxygen scavenger

Photosensitive dye oxidation is an oxygen scavenger system consisting of sealing a small coil of an ethyl cellulose film which contains a dissolved photosensitive dye and a

singlet O_2 acceptor in a transparent package. By using lights with appropriate wavelengths, the dye molecules are excited, and then pass their excitation to oxygen as it diffuses into the film from either the package headspace or from the liquid food. The excited O_2 molecules react with the acceptor and then are consumed. While the film is illuminated, the process continues until all the oxygen reacts. The reaction scheme is the following (Vermerien et al., 1999):

$$\text{Photon} + \text{dye} \rightarrow \text{dye}^* \quad (2.8)$$

$$\text{dye}^* + O_2 \rightarrow \text{dye} + O_2^* \quad (2.9)$$

$$O_2^* + \text{acceptor} \rightarrow \text{acceptor oxide} \quad (2.10)$$

$$O_2^* \rightarrow O_2 \quad (2.11)$$

where * represents an exited state of the species.

Polyketone can act as a photosensitizer. This photochemical process has some advantages because it does not need sachets in the food package, is transparent in packaging, and works regardless of humidity. The first dye used was erythrosine, which is an FDA approved food color additive, plus a color sensitizer that is bleached by light. For singlet oxygen acceptors, several materials were tested: difurylidene erythrito (DEF), tetraphenyl prophine (TPP), dioctyl phthalate (DOT), and dimethyl anthracene (DMA). However, these are not approved for food contact. This type of oxygen scavenger does not initiate in the dark. Therefore, this technique cannot be used with non-transparent film such as aluminum foil. Examples of light-activated scavengers are $Zero_2^{TM}$ (CSIRO, Australia) and OS 1000 (Cryovac Sealed Air, USA). OS 1000 is trigged when the film is exposed to ultraviolet radiation, and is useful for the horizontal thermoform/fill/seal (HFFS) process (Brody, 2001). Recently, Cryovac launched a new type of oxygen

scavenging film named OSP OS 2000 and commercialized it for use in both flexible and rigid packaging applications. The oxygen scavenger material is based on a blend of ethylene methylacrylate cyclohexenyl methyl acrylate (EMCM) and was developed by Chevron Phillips Chemical Company (Brody, 2001). The OSP system was approved by the U.S. Food & Drug Administration (FDA) in 2000, with a limitation that it could be used only as a non-food-contact layer in laminate structures, provided that it is separated from the food by one or more polymeric layers of a total thickness of at least 6 microns (0.25 mils) (Solis and Rodgers, 2001). Figure 9 shows the performance advantage of OSP™ for juice packaging.

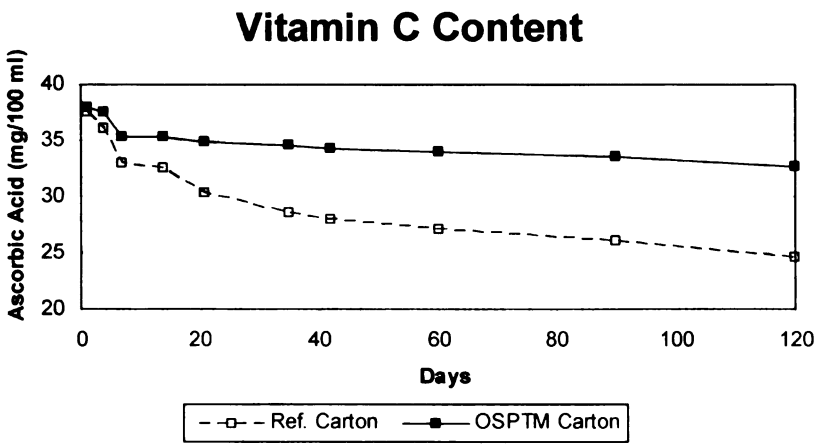


Figure 9. Performance advantage of OSP™ in juice packaging
(Source: Solis and Rodgers, 2001)

2.2.2.5. Enzyme based oxygen scavengers

Another oxygen scavenger technique uses enzyme reactions. The enzyme responds with a specific substance to scavenge incoming O_2. Glucose oxidase is a popular oxygen scavenging enzyme. Glucose oxidase transfers two hydrogens from the

-CHOH group of glucose to oxygen with the formation of glucono-delta-lactone and hydrogen peroxide. The lactone reacts with water to form gluconic acid. The reaction is the following (Vermeiren et al., 1999):

$$2G + 2O_2 + 2H_2O \rightarrow 2GO + 2H_2O_2 \qquad (2.12)$$

where G is glucose.

However, H_2O_2 is a highly oxidizing agent and therefore objectionable, so catalase is introduced to break down the peroxide:

$$2H_2O_2 + \text{catalase} \dashrightarrow 2H_2O + O_2 + \text{catalase} \qquad (2.13)$$

From the two reactions above, the original oxygen is reduced by half, and ultimately it will become zero. The glucose plus catalase enzyme system is very sensitive to pH, water activity, temperature, and various other factors. Also, it requires water for activation, so it cannot be used for low humidity products. Another disadvantage is that, when oxidation occurs, some reactions may generate undesirable odor compounds such as ketones or aldehydes (Labuza and Breene, 1989). An oxygen scavenger of this type has been commercialized by Bioka in Finland, which can be easily applied to the surface of polyolefins (Vermeiren et al., 2003).

2.2.3. Recent technologies in oxygen scavengers

Oxygen scavenging technologies are the most developed and most patented of all active packaging technologies owing to their market success. The global market for oxygen scavengers was presumed to exceed $200 million, and exceed 10 billion units in Japan, several hundred million in the USA and tens of millions in Europe in 1996. This market was estimated at $1 billion by 2001 (Day, 2003). Before 1995, more than 70 patents involving oxygen scavengers had been granted across the world (Ozdemir and Floros, 2004). Recent US patents issued for oxygen scavenging focus on technologies that are incorporated into film or sandwiched in the structure of bottles. Another trend is non-metal systems replacing metals. Despite the fact that the speed and capacity of oxygen scavenging in film are fairly low compared to the oxygen absorbing sachets, the technologies for incorporating into film offer several advantages over sachets: useful for retorting or pasteurizing products using hot water, prevention against distortion or transformation by sachet contact with products, cost saving by production efficiency that does not need a secondary package, and elimination of inadequate consumer acceptance due to fear of ingestion. For the sandwiching technologies, FDA approval for use with post-consumer-recycled polyester (PCR PET) in soft drink bottles has accelerated introduction of the oxygen scavenging system for beer bottles. This oxygen scavenger system was developed by Continental PET technologies and is composed of nylon MXD6/cobalt salt mixed with a 2% blend of polyketones to enhance the oxidation reaction. It is used as the middle layer in PET bottles (Brody et al., 2001). Constar International Inc. developed "MonOxbar Plus", a blend of Constar's patented "Oxbar" oxygen scavenger with ultraviolet-light-blocking PET. They commercialized it in a 46 oz monolayer ketchup bottle and a 750 ml wine PET container in 2008 (Constar 2004;

Kalkowski, 2008). Table 3 shows recent information about patents in the U.S.

Table 3. Recently issued US patents for oxygen scavenging systems

Company	Structure/composition	year
BP Amoco Corp.	Copolymers comprising polyester segments + polyolefin oligomer segments	2000
BP Corp.	Oxygen scavenging monolayer bottles (PET + oxygen scavenger of low migration level)	2007
Chevron Chemical Co.	Oxygen scavenger consisting of poly (ethylene-methyl acrylate) terpolymer + gable-top carton	2003
	Multilayer rigid container having oxygen scavenger selected cyclic olefinic pendent group	2006
Ciba Specialty Chem.	Oxygen scavenger for extrusion coating; oxidizable metal + polymeric resin (metallocene Polyethylene and styrene-rubber block copolymer)	2003
Cryovac Corp.	Zeolite + an oxidizable compound and a transition metal catalyst + ethylenically unsaturated hydrocarbon	2002
	Oxygen scavenging film with cyclic olefin copolymer + dosage of actinic radiation to trigger	2007
Eastman Chemical Co.	Polyamide nanocomposites (silicate material) with oxygen scavenging capability	2004
	Polyester based cobalt concentrates for oxygen scavenging compositions	2007
Honeywell International Inc.	Polyamide homopolymer + copolymer + an oxidizable polydiene or oxidizable polyether	2004
Kuraray Co.	EVOH + transition metal salt (iron, nickel, copper and cobalt salt)	2003
Mitsubishi Gas Chemical Co.	Oxygen permeating resin layer + deoxidizing resin layer containing a particulate absorbing composition + smoothing layer + gas barrier layer	2000

Table 3. (*continued*)

Company	Structure/composition	year
	Oxygen absorbing multilayer film including gas barrier epoxy containing xylyenediamine unit ($NCH_2C_6H_4CH_2N$)	2004
Otsuka Pharmaceutical	Oxygen scavenger for pharmaceutically acceptable salt (tetrazolylalkoxy-dehydrocarbostyril compound)	2004
Toyo Seikan Kaisha	Organic oxidizing component (xylylene group + polyamide) + transition metal catalyst	2005
W.R. Grace and Co.	Carrier material + metal loaded cationic exchange material	2000
	Metal catalyzed ascorbate compounds (D- or L-ascorbic acid or a salt or a fatty acid) as oxygen scavenger	2004

2.3. Regulatory issues

According to the results from the 'Actipak' research project funded by European Commission (FAIR Project CT-98-4170), at least four types of food safety and regulatory issues related to active packaging of food needed to be addressed. First, any need for food contact approval must be established before any form of active packaging is used. Second, it is important to consider environmental regulations covering active-packaging materials. Third, there may be a need for labeling in cases where active packaging may give rise to consumer confusion. Finally, it is proper to consider the effects of active packaging in the microbial ecology and safety of foods (De Kruijf, 2000).

Legislative demands regarding food packaging and food contact materials include specific consumer protection and environmental concerns. In various countries, legislation related to food contact materials has been framed. However, there are only a few specific regulations for these innovative concepts, and the basic criteria for these regulations differ between countries (Ahvenainen, 2003).

In the USA, components directly introduced in foodstuffs or indirectly introduced through packaging are regarded as food additives that are defined in Section 321 (s) of the Federal Food, Drug and Cosmetic Act. Therefore, the active ingredients have to be evaluated as additives by strict toxicological testing before use according to 21 USC Section 348 (C) (3) (A). The manufacturer must submit a filing to the Center for Food Safety and Applied Nutrition (CFSAN) to demonstrate safety (FDA, 2002). If a manufacturer does not have to file a Food Additive Petition (FAP) or a Food Contact Notification (FCN) proposed by CFSAN, the manufacturer can seek CFSAN's agreement that the substance is generally recognized as safe (GRAS).

Recently, FDA has been under increased pressure to regulate the use of nanotechnology, because research is not widely available to demonstrate the pattern of migration of active ingredients while the market is rapidly growing (Cole, 2007). The market using nanotechnology increased more than $860 million in sales worldwide in 2006, and is predicted to be a $30 billion market within 10 years (Helmut Kaiser Consultant, 2005). Oxygen scavengers using nanocomposites such as silicate or organo-clay have also been applied in the market (Hildebrandt, S., 2005; Eastman Chemical Co., 2004). For this reason, the U.S. FDA's Nanotechnology Task Force Team was organized in 2006 and released a report on the scientific and regulatory challenges related to the use of nanotechnology in products regulated by the FDA on July 23, 2007 (FDA News, 2007). The Task Force reported that the use of nanomaterials in products regulated by the FDA presents challenges similar to those products using existing technologies and other emerging technologies.

In Japan, new components must be registered as chemicals according to the Guidelines for Screening Toxicity Testing of Chemicals. Migration behavior of active packaging has not been explicitly described in any of this regulation (Day, 2003; Ahvenainen, 2003).

In Europe, only a few active packaging systems have been applied and the global market share is relatively small, because EU legislation is stricter than other countries such as USA and Japan (Climpson, 2005). Active releasing materials were not allowed before 2004 since the regulations at that time set an overall maximum migration limit of 60 mg / kg food from the packaging into food for all packaging material including active packaging. This limit was not appropriate for active releasing materials, since it is often their aim to release substances above this limit. The active systems that were not limited

by the legislation at that time were absorbing materials such as oxygen scavengers and moisture absorbers, since they complied with the legislation at that time as long as the toxicological properties and quantities of migration of the active packaging materials were acceptable (Dongen and Kruijf, 2007).

A new Framework Regulation (1935/2004/EC) including the use of active and intelligent packaging systems was adopted in 2004, and requires that they shall not endanger human health. This new Framework Regulation for Food Contact Materials is a regulation instead of the previous Directive (89/109/EEC), which focused only on food-contact materials for food packaging and mostly related to plastic materials. All new active and intelligent packaging systems initially need to be evaluated by the European Food Safety Authority (EFSA) (Cole and Bergeson, 2007). EFSA said assessments for the substance migration will focus "on the migration into food of the active or intelligent substances, and of the substances possibly generated through degradation or reactions, as well as their toxicological properties" (Byrne, 2009).

2.4. Migration from active packaging

The key regulatory issue is food-contact approval, because substances may migrate into the food from active packaging. Such migrants may be intentional or unintentional. Intentional migrants include antioxidants, ethanol and antimicrobial preservatives, which require regulatory approval in terms of their identity, concentration and possible toxicological effects. Unintentional migrants include various metal compounds or other system components that could enter the food. In most countries, there are regulations limiting or prohibiting the quantities of such components in the food. However, no specific regulations exist on testing the suitability of active and intelligent packaging systems in direct contact with foods and, in many cases, the testing protocols used are not necessarily appropriate, being based on those developed for plastic packaging materials (Robertson, 2006).

In order to solve these problems, in Europe, the Actipak project started in January 1999, and a selection of available active and intelligent systems was made for compositional analysis and overall migration study. The composition was experimentally verified by means of analytical techniques such as GC-MS, atomic absorption (AA) spectrometry, IR spectrometry, X-ray fluorescence (XRF) spectrometry and scanning electronic microscopy for energy-dispersive spectrometry (SEM-EDS). For the determination of the overall migration from the active and intelligent systems to the various food simulants, the relevant CEN EN 1186 methods were evaluated by the Actipak project in Europe (De Kruijf et al., 2002). This is similar to the method (Food-type as defined in 21 CFR 176.170 (c)) recommended by FDA (FDA, 2002). Evaluation of OS composition was focused on determining the major active components and relevant reaction products [Table 4].

Table 4. Some typical results of the evaluation of the composition of active packaging systems (Source: De Kruijf et al. 2002)

Packaging system	Ingredients identified
Oxygen scavengers	iron powder silicates sulphite chloride polymeric scavenger elements: Fe, Si, Ca, Al, Na, Cl, K, Mg, S, Mn, Ti, Co, V, Cr, P
Ethylene scavengers	plasticizer permanganate zeolite elements: Mg, Al, Si, K, Ca, Ti, Fe, Mn
Moisture absorbers	silicates plasticizer cellulose fiber sugars acids ethanol glycerol surfactant elements: Mg, Fe, Ca, K, S, Ti, P, V Mn, Cr, Zn, Sr, Si, Al, Na
Antimicrobial releasers	acids silicates ethanol zinc elements: Si, Na, Al, S, Cl, Ca, Mg, Fe, Pd, Ti

More detailed research on the migration of oxygen scavengers was done by Lopez-Cervantes and other members of the TNO Nutrition and Food Research Institute in Europe (Lopez-Cervantes et al., 2003). They studied two commercial oxygen scavenger

systems: One (OS1) had the form of a cup made of plastic and covered with a porous plasticized paper seal. The other one (OS_L) was a sachet laminated with paper and plastic. The weight and contact area of OS1 was 6.28 g and 19.6 cm^2. OS_L was 56.7 g and 68.0 cm^2. Species migrating from OS1 and OS_L which were stored for 10 days at 40℃ immersed in 200 ml liquid simulant in a hermetically sealed jar were evaluated by XRF and SEM-EDS. The major elements were identified by XRF as Na, Cl and Fe. Minor elements detected were Si, P, Ca and others. SEM-EDS revealed Na, Cl, Fe, C and O as major elements and minority structures contained Ca and Cl. They concluded that the main components of the residue were NaCl and iron compounds, and that the main migrants were therefore NaCl and iron. Samples of the simulant were then taken for determination of NaCl and iron as well as the overall migration (OM) in water and 3% acetic acid. From Table 5, it can be seen that the sum of the calculated masses of migrated NaCl and iron compound [$Fe(OAc)_2$] that was a mixture of ferric oxide, and ferric and ferrous acetate is close enough to the total migrated mass to be taken as an acceptable estimate of overall migration. Not only the quantities of overall migration, but also NaCl migrating into water and 3% acetic acid from OS1 and OS_L exceed the overall migration value of 60 mg/kg [12 mg/200 ml] set by EU legislation (European Commission, 1990). It is disputable how the limit should be applied because neither OS1 nor OS_L appear suitable for use in direct contact with these kinds of simulants. Even if they concluded that both systems should be positioned to minimize contact between their porous surfaces and packaged foodstuffs, it is not easy because oxygen scavenging systems positioned to minimize contact with food could be in contact with food during transportation or handling. Furthermore, in the case of a cosmetic which is filled in a tube, it is impossible to avoid contact with the contents. Therefore, to avoid or reduce the

quantity of migration below the value of 60 mg/kg, a new concept for the packaging system such as a multilayer film which incorporates an oxygen scavenger in the core-layer structure is needed.

On the other hand, since proper simulants have not been identified for most of the pharmaceuticals or cosmetic products, food simulants have been used for pharmaceuticals and cosmetics (Figge et al., 1978).

Table 5. Comparison of overall migration (OM) into water and 3% acetic acid, as calculated from total final residue mass, with specific migration of NaCl and Fe (the latter as $Fe(OAc)_2$), as calculated from observed migration of chloride and iron, respectively. (Source: Lopez-Cervantes et al., 2003)

Unit: mg/200ml

OS element	Simulant	NaCl	$Fe(OAc)_2$	NaCl+$Fe(OAc)_2$	OM
OS1	water	88 ± 6	0	88 ± 6	107 ± 9
	3% HAc	72 ± 12	654 ± 67	726 ± 68	707 ± 17
OS_L	water	821 ± 8	3 ± 0.1	824 ± 8	898 ± 6
	3% HAc	968 ± 86	688 ± 69	1656 ± 110	1263 ± 56

2.5. Advances for active packaging

As mentioned above, active packaging systems are already being successfully commercialized to extend shelf life in the U.S. and Japan. However, in Europe and other countries, only a few of these systems are in use and the global market share is relatively small (Dongen and Kruijf, 2007). The main reason is that EU regulation was tighter than those of other countries, and the rest, including Korea, do not have any regulation for this system. Therefore, when they do the future work not only to remove legislative barriers or establish proper safety regulations, but also to provide reliable information channels to consumers and realize economic advantages by using these technologies, many new opportunities in the food and non-food industries will arise and a bright future for active packaging can be expected. For the successful accomplishment of this work, some issues identified by the Actipak project in Europe are useful for consideration in other countries as well as in Europe (Robertson, 2006).

2.5.1. Major issues identified by Actipak

The Actipak project (ACTIPAK-FAIR CT98-4170) was carried out by twelve people from research institutes such as TNO in the Netherlands and industrial development centers to establish active and intelligent packaging systems within the relevant regulations in Europe (Ahvenainen, 2003; De Kruijf et al., 2002). This resulted in the adoption of a new Framework Regulation (1935/2004/EC, which was published on 27 October 2004). Some factors Actipak identified to be considered in the development of active packaging in the future (De Jong et al., 2005) are:

1) Several legal barriers: Active packaging concepts are already commercialized in many countries such as the USA and Japan, but they cannot be used widely in Europe yet, due

to legislative restrictions.

2) Reliability and effectiveness: All active systems should be thoroughly validated for each specific application to be sure that they are effective.

3) Economic issues: In order to expand active packaging, cost reduction is still a very important issue to solve.

4) Acceptance by consumers, food producers and retailers: it is necessary to provide reliable information to reduce the consumer resistance, and lack of knowledge about effectiveness.

2.5.2. Selection of an appropriate oxygen scavenger

As oxygen scavengers are also one of the major components in active packaging, design of active packaging should satisfy some requirements as well as the considerations mentioned in the upper section 2.5.1. They should

1) Be harmless to the human body. Especially, in the case of sachets, they should provide clear information to consumers that oxygen absorbers are not food or food additives because there is the possibility of accidents.

2) Be designed so that the speed and capacity of the oxygen scavenger are appropriate for the shelf life of the products.

3) Not produce toxic substances or undesirable gases or off-flavors.

4) Be economically priced.

2.5.3. Package design and process control

In consideration of processing technologies, polymeric materials containing oxygen scavenging components should have good processability, and be useful to

incorporate into appropriate packaging materials, and have high compatibility with commercialized polymers that are used in packaging design. The oxygen scavenging materials and packages such as film, bottles and other packaging must be kept in a stable condition and protected from premature activity. The most suitable packaging design is that the packaging materials and structures, especially the oxygen scavenging layer, are not deprived of their physical properties after the process of oxygen scavenging. Moreover, they should not generate any kinds of byproducts that can affect the sensory qualities such as off-flavor or change in nutritional properties of the packaged products (Lopez-Rubio, 2004).

2.6. References

Ahvenainen, R., *Novel food packaging techniques*, Woodhead Pub., Abington Cambridge, England, pp. 5-21, 2003.

Berenzon, S., and I.S. Saguy, "Oxygen absorbers for extension of crackers shelf-life," Food Science and Technology, 31: 1-5, 1998.

Bharat Book Bureau, "Active & intelligent packaging forecasts for 2011 & 2016," Aug. 2007. www.bharatbook.com/derail.asp?id=51185, (accessed Jan. 12, 2008).

Bohrer, Timothy H. and Richard K. Brown, "Packaging Techniques for Microwaveable Foods," in Ashim K. Datta and Ramaswamy C. Anantheswaran, ed., *Handbook of Microwave Technology for Food Applications*, Maecel Dekker, Inc., New York, NY, pp. 397-469, 2001.

BP Corp. (Inventors: Tibbitt, J.M., P.J. Cahill, G.E. Rotter, D.P. Sinclair, G.T. Brooks, R.T. Behrends), "Oxygen scavenging monolayer bottles," U.S. Patent 7214415, May 8, 2007.

Brody, A.L., E.R. Strupinsky, Kline L. R., *Active Packaging for Food Applications*, Technomic Pub., Lancaster, PV, PP. 11-86, 2001.

Byrne, Jane, "Views sought in novel packaging review," Decision News Media SAS, Feb. 26, 2009. www.foodproductiondaily.com/content/view/print/237863

Caba Specialty Chem. (Inventors: Chiang, W.L., B.C. Tsai, S.Y. Chen, L.N. Venkateshwaran), "Oxygen-scavenging compositions and articles," U.S. Patent 6586514, Jul. 1, 2003.

Chevron Chemical Co. (Inventors: Cai, G., T.Y. Ching, H. Yang), "Container having oxygen-scavenging core layer," 7056565. Jun. 6, 2006.

Chevron Chemical Co. (Inventors: Jerdee, G.D., J.P. Leonard, T.Y. Ching, J.L. Goodrich, B.D. Rodgers, R.P. Schmidt), "Oxygen scavenging packaging," U.S. Patent 6569506, May 27, 2003.

Climpson, J., "Global markets for active packaging in 2001, 2005, and 2010" in Pira International Leatherhead report, *The Future of Active Packaging in Food and Drink Markets,* Surrey, UK, 2005.

Cole, Michael F. and Lynn L. Bergeson, "Regulation of new forms of food packaging produced using nanotechnology" " in Charles L. Wilson, ed., *Intelligent and Active Packaging for Fruit and Vegetables*, CRC Press, Taylor & Francis Group, Boca Raton, FL, pp. 289-306, 2007.

Constar International Inc, "MonOxbar™," PET Oxygen Barrier Effectiveness: A Comparison of Alternatives" in Proceedings of Pack Expo, 2004. www.constar.net.

Cryovac Corp. (Inventors: Rivett, J.W. and D.V. Speer), "Oxygen scavenging film with cyclic olefin copolymer," U.S. Patent 7258930, Aug. 21, 2007.

Day, B.P.F., "Active packaging," in Richard Coles et al. ed., *Food Packaging Technology*, Blackwell Pub., London, pp. 282-302, 2003.

Day, B.P.F., "Underlying principles of active packaging technology," *Food Cosmetics and Drug Packaging*, 23: 134-139, 2000.

De Jong, A.R., H. Boumants, T. Slaghek, J. Van Veen, R. Rijk, & M. Van Zandvoort, "Active and intelligent packaging for food: Is it the future?," *Food Additives and Contaminants*, 22: 975-979, 2005.

De Kruijf, N., M. van Beest, R. Rijk, T. Sipiläinen-Malm, P. Paseiro Losada and B. De Meulenaer, "Active and intelligent packaging: applications and regulatory aspects," *Food Additive and Contaminations*, 19: 144-162, 2002.

Dongen, William D., and Nico de Kruijf, "ACTIPAK in Europe" " in Charles L. Wilson, ed., *Intelligent and Active Packaging for Fruit and Vegetables*, CRC Press, Taylor & Francis Group, Boca Raton, FL, pp. 315-327, 2007.

Eastman Chemical Co. (Inventors: Bernard, L.G., H.Clauberg, M.J. Cyr, W. Gilmer, J.T. Owens, M.E. Stewart, S.R. Turner, S. Basrodia, J. Christopher, Matayabas, Jr.), "Polyamide nanocomposites with oxygen scavenging capability," U.S. Patent 6777479, Aug. 17, 2004.

Eastman Chemical Co. (Inventors: Stewart, M.E., E.E. Sharpe, Jr., B.B. Gamble, S.L. Stafford, R.N. Estep, J.C. Williams, T.R. Clark), "Polyester based cobalt concentrates for oxygen scavenging compositions," U.S. Patent 7288586, Oct. 30, 2007.

European Commission, "Directive 90/128/EEC of 23 February 1990 relating to plastic materials and articles intended to come into contact with foodstuffs." *Official Journal of European Communities*, L349; 26-47, 1990.

Farkas, J.K., "The development of iron-based oxygen absorbing systems used in food packaging and preservation," Ph.D. dissertation, Purdue University, West Lafayette, AAT 9953735, 1998.

Farrell, C.J., and B.C. Tsai, "Oxygen scavenger," U.S. Patent 4702966, Oct. 27, 1987.

FDA (U.S. Food and Drug Administration), "Guidance for Industry: Preparation of Food Contact Notification: Administrative, FINAL GUIDANCE," May 2002. http://www.cfsan.fda.gov/~dms/opa2pmna.html#II-B, (accessed Mar. 18, 2008).

FDA (U.S. Food and Drug Administration), "FDA Regulation of Nanotechnology Products". www.fda.gov/nanotechnology/regulation.html, (accessed April 10, 2009).

FDA News, "FDA Nanotechnology Report Outlines Scientific, Regulatory Challenges," July 25, 2007. http://www.fda.gov/nanotechnology/taskforce/report2007.pdf, (accessed. April 10, 2009).

Figge, K., J. Koch and W. Freytag, "The suitability of simulants for foodstuffs, cosmetics and pharmaceutical products in migration studies," *Food and Cosmetics Toxicology*, 16 (2): 135-142, 1978.

Gill, C.O., and J.C. McGinnes, "The use of oxygen scavengers to prevent the transient discoloration of ground beef packaged under controlled oxygen-depleted atmospheres," *Meat Science*, 41: 19-27, 1995.

Honeywell International Inc. (Inventors: Akkapeddi, M.K., T.J. Kraft, E.P. Socci), "Oxygen scavenging high barrier polyamide compositions for packaging applications," U.S. Patent 6685861, Feb. 3, 2004.

Helmut Kaiser Consultancy, "Nanotechnology Makes Packaging Intelligent, Smart and Safe," May 26, 2005. www.nanotechwire.com/news.asp?nid=1961&pg=9, (accessed Feb. 10, 2008).

Hilderbrandt, S., "Nanocomposites Improve Package Properties," 2005. www.uwstout.edu/rs/2005/article1.pdf, (accessed Jan. 7, 2009).

Hotchkiss, J.H., "Safety considerations in active packaging," in Rooney, M. L., ed., *Active Food Packaging*, Blackie Academic and Professional, London, pp. 238-255, 1995.

Hurme, E. and R. Ahvenainen, "Active and smart packaging of ready-made foods," in Proceedings of the International Symposium on Minimal Processing and Ready Made Foods, SIK, Sweden, pp. 4-7, 1996.

Insider, "FDA Falls Behind on Nanotech Dietary Supplements," Jan. 15, 2009. www.naturalproductsinsider.com/articles/fda-way-behind-onnanotech--dietary-supplemen.html,

Kalkowski, J., "Frech winemaker finds marketing success in PET bottles as alternative packaging that helps it sustain a commitment to environmental protection," *Packaging Digest,* Oct. 1, 2008.

Klein, T., and D. Knorr, "Oxygen absorption properties of powered iron," 55: 869-870, 1990.

Koyama, Masayasu, Y. Oda, and M. Yamada, "Plastic multilayer vessel," U.S. Patent 5153038, Oct. 6, 1993.

Kuraray Co. (Inventors: Tai, S., H. Shimo, M. Nakaya, H. Takamatsu, M. Maeda), "Oxygen absorptive resin composition," U.S. Patent 6599598, Jul. 29, 2003.

Labuza, T.P., and W.M. Breene, "Applications of 'active packaging' for improvement of shelf life and nutritional quality of fresh and extended shelf life foods,' *J. Food Process. Preserv.*, 13: 1-69, 1989.

Lopez-Cervantes, J., D.I. Sanchez-Machado, S. Pastorelli, R. Rijk and P. Paseiro-Losada, "Evaluation the migration of ingredients from active packaging and development of dedicated methods: a study of two iron-based oxygen absorbers," *Food additives and contaminants*, 20: 291-299, 2003.

Lopez-Rubio, A., E. Almenar, P. Hernandez-Munoz, J.M. Lagaron, R. Catala and R. Gavara, "Overview of Active Polymer-Based Packaging Technologies for Food Applications," *Food Review International*, 20(4): pp. 357-387, 2004.
Mitsubishi Gas Chemical Co. (Kashiba, T., S. Kihara, T. Kutsuna, "Oxygen-absorbing multi-layer film)," U.S. Patent 6746772, Jun. 8, 2004.

Otsuka Pharmaceutical (Inventor: Hong, K.W.), "Active oxygen scavenger," U.S. Patent 6743806, Jun. 1, 2004.

Ozdemir, M. and J.D. Floros, "Active Food Packaging Technologies," *Food Science and Nutrition,* 44: 185-193, 2004.

PET planet insider, "Materials/ Recycling: Multi-Layer +," Aug. 2000. http://www.hbmedia.net/petplanet/petplanet/insider/2000/08/articles/materialsrecycling3.shtml, (accessed Jul. 7, 2008).

Reynolds G., "Active & intelligent packaging to reach $1.1 billion by 2011," *PackWire*, Aug. 30, 2007. www.packwire.com/news/ng.asp?id=79381-freedonia-pet-oxygen, (accessed Apr. 17, 2008).

Rijk, R., M. Van Beest, N. De Kruijf, K. Bouma, C. Martin, B. De Meulenaer and T. Sipiläinen-Malm, "Active and intelligent packaging systems and the legislative aspects?," *Food Packaging Bulletin*, 10(9 & 10), pp. 2-10, 2002.

Robertson, G.L., *Food Packaging: Principles and Practice*, 2nd ed., Taylor & Francis/ CRC Press, Boca Raton, FL, pp. 285-311, 2006.

Selke, Susan. E.M., John D. Culter, Ruben J. Hernandez, *Plastic Packaging*, 2nd Hanser Pub., Munich, pp. 144-147, 2004.

Smith, J.P., B. Ooraikul, W.J. Koersen, E.D. Jackson and R.A. Lawrence, "Novel approach to oxygen control in modified atmosphere packaging of bakery products," *Food Microbiology*," 3: 315-320, 1986.

Solis, J.A. and B.D. Rodgers, "Factors affecting the performance of new oxygen scavenging polymer for packaging applications," *Journal of Plastic Film & Sheet*, 17: 339-349, 2001. http://intl-jpf.sagepub.com/cgi/reprint/17/4/339.pdf, (accessed Feb. 3, 2008).

TNO Nutrition & Food Research et al., "ACTIPAK FAIR-CT 98-4170," 2002. http://www.packagingvalley.com/files/FINAL%20ACTIPAK.pdf, (accessed Jan. 16, 2008).
Toyo Seikan Kaisha (Inventors: Kikuchi, A., I. Komatsu, T. Yamada, Y. Kitano, G. Saito), "Resin composition and multi-layer container using the same," U.S. Patent 6878774, Apr. 20, 2005.

UNCTAD/ WTO, "Active Packaging and Susceptors," *Packdata Factsheet No.5*, 1992. http://www.intracen.org/Tdc/Export%20packaging/PAFA/English/pafa05eng.pdf, (accessed Jun. 5, 2008).

Vermeiren, L., F. Devilieghere, M. van Beest, N. De Kuijf, and J. Debevere, "Developments in the active packaging of foods," Trends Food Sci. Technol., 10: 77-86, 1999.

Vermeiren, L., L. Heirlings, F. Devilieghere and J. Debevere, "Oxygen, ethylene and other scavengers," in Raija Ahvenainen, ed., *Novel Food Packaging Techniques*, Woodhead Pub., Abington Cambridge, England, pp. 22-49, 2003.

W.R. Grace and Co. (Inventors: Teumac, F.N., B.D. Zenner, B. A. Ross, L.A. Deardurff, M.R. Rassouli), "Metal catalyzed ascorbate compounds as oxygen scavengers," U.S. Patent 6709724, Mar. 23, 2004.

3. DEVELOPMENT OF MULTILAYER FILM INCORPORATING OXYGEN SCAVENGER

3.1. Introduction

As mentioned in section 1.3, one of the most important factors in developing commercial products and packaging to contain vitamin A compounds such as retinol is how to prevent the decomposition from oxygen (Barua and Hrold, 1998; Ball, 2006). Oxygen scavenging technology seems to solve the problem because it can effectively remove oxygen from the inner package environment (Ozdemir and Floros, 2004). Among the several active components that absorb oxygen, iron based material is most commonly used. Recently, the incorporation of oxygen scavengers in the middle layer of a multilayer film has been seen as a better way of resolving problems such as that the oxygen scavengers in a monolayer film are direct contact with products and that sachet types are not appropriate in tube type containers because of inserting or tagging problems (De Jong et al., 2005; Robertson, 2006).

The research of Foltynowicz shows that small particles of oxygen scavengers tend to agglomerate. This agglomeration is the clumping together of small particles of oxygen scavengers, which occurs during the extrusion process. The oxide layer, which forms on the surface of the agglomerates on exposure to oxygen, hinders further oxygen access to the bulk scavenger and results in a decrease of oxygen uptake (Foltynowicz, et al., 2002). It also influences the mechanical properties because of uneven bubble shape caused by agglomerations in the film during the blown film process. Therefore, another major factor is how to make oxygen scavenging multilayer films without any agglomerations, because they can reduce not only the mechanical and thermal properties but also the oxygen

absorbing capacity.

Thus, the first objective of this study is to develop a multilayer film incorporating iron based oxygen scavenger as follows:

1) To design a proper multilayer structure and process conditions

2) To have the best value for mechanical, optical and thermal properties

3) To evaluate the oxygen absorbing capacity in multilayer films

3.2. Materials and methods

3.2.1. Experimental work

3.2.1.1. Film design and material selection

The film was designed with a three-layer structure and manufactured by a co-extrusion blown film process which has three extruders. The inner and outer layers were composed of high density polyethylene (HDPE) and the core layers were an oxygen scavenging material mixed with the same HDPE as used in the inner and outer layers. Oxygen scavenging materials (OS1 and OS2) were compounded iron powders with polyethylene as a base resin, and the oxygen uptake capacity (cc O_2/g) was designed to have the same value. They were all commercialized products; OS1 was received from a company in Europe, and OS2 was purchased from a Japanese company.

To improve dispersion of oxygen scavenger in the film, linear low density polyethylene (LLDPE) was used instead of HDPE, which had resulted in some agglomerations during processing the film. The polymers selected for the investigation are all commercialized materials and are listed in Table 6.

The total thickness of the film that was designed experimentally was 130 ~ 225 ㎛. The thickness of the inner and outer layers which consisted of LLDPE or HDPE were approximately 25 ~ 30 ㎛, and the middle layer which consisted of oxygen scavengers was 75 ~ 175 ㎛. In order that oxygen scavenging materials of the middle layer do not contact the product directly, the inner layer must be designed to be at least 12.5 ㎛ (0.0005 inch) thick (plastic film) and 25 ㎛ (0.001 inch) thick (plastic sheet) for the material in the middle to be considered generally recognized as safe (GRAS) by the U.S. FDA (Brody et al., 2001).

Table 6. Characteristics of the materials selected

Material	Commercialized Country	Melt Index (g/10 min) ASTM D1238	Density (g/cc) ASTM D1505	Registration
OS1	Europe	3.0	1.42	US FDA, US TSCA, ECCS,
OS2	Japan	5.0	1.38	MHW, GSTTC
LLDPE	Korea	1.0	0.928	US FDA
HDPE	Korea	0.07	0.956	US FDA

US FDA: United State Food and Drug Administration
US TSCA: United State Toxic Substances Control Act
ECCS: European Community Compliance Statement
MHW: Ministry of Health and Welfare (JAPAN)
GSTTC: Guideline for Screening Toxicity Testing of Chemicals

1) Calculation for weight of oxygen scavenger

Before making the desired oxygen scavenging film, it was necessary to calculate the weight of oxygen scavenger needed in the middle layer of the film. In order to determine the required content of oxygen scavenger, the volume in the headspace of the package was measured by using a syringe to inject water into the headspace of a packaged product. The average air volume of the headspace (Va) was 5.2 cc. Then, the volume of oxygen present in the headspace of the package (Vo) could be calculated as follows:

$$Vo = Va \times [O_2] / 100 = 5.2 \text{ cc} \times 21 / 100 = 1.09 \text{ cc} \quad (3.1)$$

$$M = Vo / Co = 1.09 \text{ cc} / 18 \text{ cc/g} = 0.061 \text{ g} \quad (3.2)$$

where, $[O_2]$: initial O_2 concentration in package (= 21% if air)

M: needed weight of oxygen scavenger material

Co: oxygen uptake capacity (18 ccO_2/g), OS1 and OS2 had the same values.

2) Calculation for film thickness of oxygen scavenging layer

From the equation (3.2), the needed weight of oxygen scavenger materials to absorb fully the oxygen in the headspace of the package was 0.061 g. In order to incorporate the materials (0.061 g) in the middle layer of the film, the desirable film thickness of the middle layer (Tmi) was calculated using the following equation:

$$M = Sh \times Tm \times D \quad (3.3)$$

Rearranging to solve for Tmi,

$$Tmi = M / (Sh \times D) \quad (3.4)$$

where Sh is the interior surface area of the headspace in the package.

$$Sh = 2\pi r \times h = (2 \times 3.1416 \times 1.22\ cm) \times 2.0\ cm$$

$$= 7.67\ cm \times 2.0\ cm = 15.34\ cm^2 \quad (3.5)$$

where h is the interior height of the headspace in the package (2.0 cm).

Since most of the residual oxygen was located in the headspace of the package, Sh was calculated instead of S (total interior surface of the package). D was the density of the middle layer.

For film having different formulations, such as when the formation of the middle layer was changed by adding LLDPE or HDPE resin into the oxygen scavenger material (M = 0.061 g), the desirable film thickness (Tmi) was calculated using the following equation:

$$Tmi = Mi / (Sh \times Di) \quad (3.6)$$

where Mi is the weight of the blend of LLDPE or HDPE with the oxygen scavenger material (M = 0.061 g), Di is the new density of the blend with LLDPE or HDPE.

In the case where HDPE was added 70 wt % into OS1 that had 0.061 g of oxygen scavenger material, the ratio of OS1 was 30 wt %, Tmi was calculated as follows:

$$Tmi = \frac{Mi}{Sh \times Di} = \frac{\frac{M}{OS1wt\%}}{Sh \times [(1 - OS1wt\%) \times HDDi + OS1wt\% \times OS1Di]}$$
$$= \frac{\left[\frac{0.061g}{0.3}\right]}{(15.34cm^2) \times [(1-0.3) \times 0.956g/cm^3 + 0.3 \times 1.42g/cm^3]} \quad (3.7)$$

= 0.01210 cm = 121.0 μm

where HDDi was the density of HDPE, and OS1Di was the density of OS1.

When LLDPE was added 50 wt % into OS2 that has 0.061 g of oxygen scavenger material, the ratio of OS2 was 50 wt %, T_{mi} was calculated as follows:

$$Tmi = \frac{Mi}{Sh \times Di} = \frac{\frac{M}{OS2wt\%}}{Sh \times [(1 - OS2wt\%) \times LLDi + OS2wt\% \times OS2Di]}$$
$$= \frac{\left[\frac{0.061g}{0.5}\right]}{(15.34cm^2) \times [(1-0.5) \times 0.928g/cm^3 + 0.5 \times 1.38g/cm^3]} \quad (3.8)$$

= 0.00689 cm = 68.9 μm

where LLDi was the density of LLDPE, and OS2Di was the density of OS2.

When the ratios of OS1 or OS2 and HDPE or LLDPE were changed, the desirable film thicknesses in the middle layer were changed as shown in Table 7.

Table 7. Desirable film thicknesses in middle layer

Components of middle layer					Di Average Density	Mi Middle layer film weight	Tmi Middle layer film thickness
No.	HDPE (wt %)	LLDPE (wt %)	OS1 (wt%)	OS2 (wt%)	(g/cm^3)	(g)	(μm)
D0	0		100		1.420	0.061	28.0
D1	50		50		1.188	0.122	66.9
D2	60		40		1.142	0.152	87.1
D3	70		30		1.095	0.203	121.0
D4	75		25		1.072	0.244	148.4
D5		50	50		1.174	0.122	67.7
D6		50		50	1.154	0.122	68.9

3.2.1.2. Experimental film structures

In order to develop a good active package, it is most important to make a good functional film. For this purpose, several kinds of films were tested. The first step was to determine the amount of agglomeration in the films because this could affect the oxygen scavenging capacity. The next step was to evaluate the appearance and properties of the films. To determine the agglomeration, HDPE and OS1 resin were blended and processed, and are shown from A to D in Table 8. However, the results of evaluating the samples for agglomeration were very poor as shown in Figure 12, so the films E and F in Table 8 were produced as a second trial. The thickness of films using LLDPE was adjusted slightly from HDPE based films, as shown in Table 8. To compare properties of the two oxygen scavenger materials (OS1 and OS2), the films were produced using the same process conditions.

Table 8. Design for each layer of films

(Unit: ㎛)

No	Inner Layer	Core Layer			Outer Layer	Total
	Material Thick.	Material	Thick. Min[1]	Design[2]	Material Thick.	Thick.
A	HDPE 25	*HDPE(50%)+**OS1**(50%)	66.9	80	HDPE 25	130
B	HDPE 25	*HDPE(60%)+**OS1**(40%)	87.1	105	HDPE 25	155
C	HDPE 25	*HDPE(70%)+**OS1**(30%)	121.0	145	HDPE 25	195
D	HDPE 25	*HDPE(75%)+**OS1**(25%)	148.4	175	HDPE 25	225
E	LLDPE 30	LLDPE(50%)+**OS1**(50%)	67.7	75	LLDPE 30	135
F	LLDPE 30	LLDPE(50%)+**OS2**(50%)	68.9	75	LLDPE 30	135

[1] : Calculated theoretical thickness

[2] : Margin-added thickness (~10 - 20% surplus over theoretical thickness)

*: Melt-blending was done in a co-rotating twin screw extruder with a 30 mm screw diameter and 30:1 L:D ratio outfitted with 2 vent ports.

3.2.1.3. Processing conditions

The 6 kinds of films in Table 8 were produced using a co-extrusion blown film line that had 3 extruders. The film line is shown in Figure 10 and the specifications of the film line are shown in Table 9. Two process conditions were used. The first condition was used for HDPE blended polymers, and the second for LLDPE blended polymers. The processing conditions for A, B, C and D in Table 8 are shown in Table 10-1, and E and F are shown in Table 10-2.

Table 9. Specification of blown film line

Extruder	Screw Dia.(mm)	Output (kg/hr)
Inner Layer	65	75
Core Layer	90	150
Outer Layer	65	75
Total Output		300

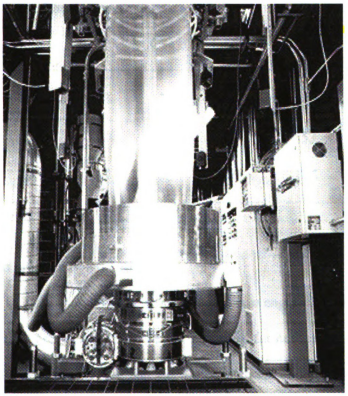


Figure 10. Co-extrusion blown film line (Reifenhäuser, Germany)

Table 10-1. Condition 1: Processing temperatures for HDPE blended polymers

Layer	Unit	Barrel in Extruder				Screen Changer	Adapter	Die
		C1	C2	C3	C4			
Inner	℃	145	149	153	157	160	165	163
Core	℃	148	154	166	170	170	172	163
Outer	℃	149	152	154	158	160	165	163

Table 10-2. Condition 2: Processing temperatures for LLDPE blended polymers

Layer	Unit	Barrel in Extruder				Screen Changer	Adapter	Die
		C1	C2	C3	C4			
Inner	℃	130	133	136	140	145	150	148
Core	℃	133	137	142	148	153	160	148
Outer	℃	130	133	136	140	145	150	148

3.2.1.4. Film preparation and sampling

The LLDPE monolayer film and oxygen scavenger (OS1 and OS2) containing multilayer films previously prepared were used for further testing of appearance, optical, thermal and mechanical properties. All films were kept at dry conditions (under 40% RH) through nitrogen gas purging for 2 min and sealed in aluminum laminated pouches after they were made. All packaged sample films were stored at 23 ℃. Each sample was collected by cutting five pieces from the film after unwinding 2 m of each stored film.

3.2.2. Evaluation of appearance and optical properties

3.2.2.1. Microscopy

Although the manufacturer claims that 1 g of oxygen scavenger material can remove 18 cc of oxygen, the efficiency can be reduced due to particle agglomeration (Brody et al., 2001). Therefore, it is necessary to determine the amount or presence of agglomeration in the film before performance tests. The testing method was to count the numbers of agglomerates in 5 samples (10 cm x 10 cm) which were cut randomly from the film. Agglomerations and the detailed images of the agglomeration were captured with a stereo microscope (Model SMZ-U, Nikon, Japan) equipped with a 35 mm camera. A 2x objective lens at 10 x zoom magnification and 2.5 x camera relay gave a 50 x final magnification of the samples. A stage micrometer was used to measure sizes of the images.

3.2.2.2. Scanning electron microscopy (SEM)

A scanning electron microscope (SEM), model 2020 configured with a lanthium hexaboride (LaB6) filament, manufactured by ElectroScan (FEI company, Hillsboro, Oregon) was used to observe the morphology of multi-layer films incorporating oxygen scavenging material in the middle layer. The acceleration voltage ranged between 10 and 20 KeV, while the water vapor pressure ranged between 2 and 3 Torr. The specimens were examined in their natural state (no conductive coating).

3.2.2.3. UV/VIS spectrometer

In order to compare the transparency (% light transmission) between oxygen scavenging films, the transmission of visible and UV light was measured with a Perkin

Elmer Lambda 25 UV/VIS Spectrometer from Perkin Elmer, Wellesley, MA. The samples were measured from 190 nm to 800 nm using an integrating sphere, and scan speed was 480 nm/min. Samples used films E and F. LLDPE film was used as a control sample.

3.2.3. Evaluation of thermal properties

3.2.3.1. Differential Scanning Calorimetry

A differential scanning calorimeter (DSC Q 100, TA Instruments, DE) was used to determine the thermal transitions of films E and F containing oxygen scavenging materials according to ASTM D-3418, and then calculate the % crystallinity, which may influence the rate of migration. These experiments were performed at a heating and cooling rate of 10℃/min from -80 ℃ to 180 ℃ using hermetically-sealed aluminum pans. The weight of the samples was approximately 8 mg and the nitrogen gas flow rate was 70 ml/min.

3.2.3.2. Thermo Gravimetric Analysis

A thermo gravimetric analyzer (TGA 2950, TA Instruments, DE) was used to determine the weight of the iron powders in the oxygen scavenging materials in films E and F, and LLDPE film was used as a control. The initial weight of the samples was approximately 3 mg. Experiments were performed in platinum pans at a ramp rate of 10 ℃/min under nitrogen purge flow (70ml/min) from room temperature to 600 ℃.

3.2.4. Mechanical properties

The tensile strength, modulus of elasticity and the percent elongation of different

film samples, which were composed of LLDPE, OS1 and OS2 films, were measured by a Universal Tester (Instron) model 5565 (Norwood, MA). Five specimens of each film were used, and the testing procedure was performed in accordance with the ASTM standard method for thin plastic film (D882A - 97). A sample width of 1 inch and initial grip gap of 2 inches with a grip separation speed of 20 in/min were used.

3.2.5. Oxygen absorbing capacity

Samples that were made of 50/50 (oxygen scavenging material/LLDPE resin), 30/70 and 20/80 blends in the core layer of the films were prepared by cutting and weighing 4.0 g of film. The film was folded and placed in a clean pint (550 cc) glass canning jar. A 1 ounce (35 ml) wide mouth vial containing 15 ml of deionized water was added to produce 100 % relative humidity in the jar. An upper glass bowl was capped with a sealing lid that contained a septum. The upper bowl and lower jar were tightly sealed to each other with grease oil and a stainless steel band [Figure 11]. The oxygen content in the air on day 0 was tested and recorded by extracting air from the cap through a septum in the seal lid. The oxygen content in the jar was tested and recorded using an Oxygen Headspace Analyzer Model-3500 (Illinois Instruments). The jar with the test film and water vial was stored at 22 ℃ for 30 days.

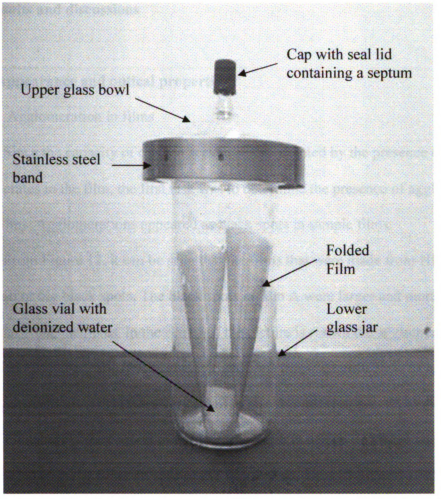


Figure 11. A pint canning jar to measure the oxygen absorbing capacity

3.2.6. Statistical Analysis

Statistical evaluation of the data was performed using SPSS (SPSS Inc., 2004). Significance levels were reported at the 95 % confidence level ($p < 0.05$) using Tukey's honestly significant difference (HSD) multiple comparison. The results of statistical analysis are shown as mean values $\pm$ standard deviation.

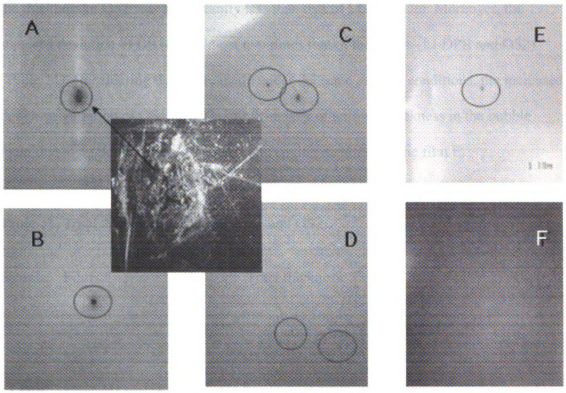
3.3. Results and discussions

3.3.1. Appearance and optical properties

3.3.1.1. Agglomeration in films

Since the capacity of oxygen scavengers is affected by the presence of agglomerates in the film, the first task was to determine the presence of agglomerations in the films. Agglomerations appeared as black spots in sample films.

From Figure 12, it can be seen that the films that were made from HDPE resin all had small or big black spots. The black spots in film A were larger and more numerous than in any other samples. In the center of the picture is shown the agglomeration magnified 400 times. The black spots in the film D that used only 25 % of oxygen scavenger materials (OS1) were very small in size, but still present. From the films A, B, C and D, the higher the content of oxygen scavenger materials, the more agglomerations were generated in the films. In case of the film B that was made of 60 % HDPE with 40 % oxygen scavenger material (OS1), small or big black spots were observed, even after melt-blending the polymer in a co-rotating twin screw extruder for better dispersion of the oxygen scavenging material. Films E and F were produced at the same production conditions and same base material (50% of LLDPE resin), but used different oxygen scavenging materials (OS1 and OS2). While the black spots appeared in film E, they were not observed in film F.



Black spots in ⬭ : agglomerations of particles
Figure 12. Agglomerations in various oxygen scavenging films

Consequently, it seems that OS2 is preferred to make a blown film at the selected conditions. Studies on improving the process conditions or techniques related to OS1 are left for future work. As a result, film F was adopted as the oxygen scavenging film to make the active packaging for this project.

3.3.1.2. Total thickness of films

The average total thickness of the LLDPE films was 135.9 ㎛/㎛ and the standard deviation was 5.92 ㎛. The thickness of OS2 was in the middle as 131.7 ± 7.062 ㎛ among the three films, and OS1 had the lowest average total thickness, 126.2 ㎛ ±12.89 ㎛. While the thickness of OS2 was not significantly different from either OS1 or LLDPE,

the thickness of OS1 was significantly less than that of LLDPE film. Moreover, the standard deviation of OS1 was almost two times that of the others (LLDPE and OS2) [Table 11]. Considering they were made under the same process conditions, the increased thickness variation of OS1 might result from lack of uniform thickness in the bubble foam due to agglomerations of oxygen scavenging materials in the film E.

Table 11. Total thickness of LLDPE, OS1 and OS2

Sample	Film	Total thickness	
		(mil)	(㎛)
LLDPE	Control	5.35 ± 0.233 [a]	135.9 ± 5.92
OS1	Film E	4.97 ± 0.507 [b]	126.2 ± 12.89
OS2	Film F	5.17 ± 0.309 [ab]	131.7 ± 7.06

Mean ± standard deviation, n = 30
Different letters within a column are significantly different ($p < 0.05$)

3.3.1.3. Morphology of the film

A cross-sectional image of film F is shown in Figure 13. The film consists of LLDPE (31 ㎛)/LLDPE + OS2 (74 ㎛)/LLDPE (32 ㎛) and its total thickness was 137 ㎛. This sample was somewhat thicker than the average total thickness of film F, but it was within ± 1σ. The particles of oxygen scavenger were well dispersed in the LLDPE matrix layer and most of the particle sizes were smaller than 10 ㎛.

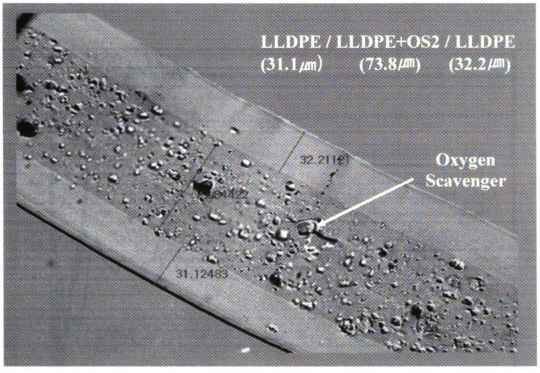


Figure 13. Cross-sectional image of film F: The middle layer is 50 wt% of OS2 resin mixed with 50 wt% of LLDPE resin.

3.3.1.4. Transparency

LLDPE (Control film), OS1 (Film E) and OS2 (Film F) were scanned from 190 am to 800 nm by a UV/VIS spectrometer, with scan speed of 480 nm/min. The value of each sample is shown in Figure 14. LLDPE shows the highest value in % light transmission, and the value of OS2 was much lower than OS1. After 400 nm, while LLDPE shows around 95 %, OS1 shows near 80 % but OS2 shows below 40 %.

One more interesting thing is that while the average % light transmission of OS1 was a little lower than that of LLDPE, the value of OS2 was much lower than that of OS1 or LLDPE. It seems that the transparency of OS2 was dramatically reduced by the good dispersion of oxygen scavenger without any agglomeration and the bigger particle sizes than those of OS1, which can interrupt the light transmission [Figure 15].

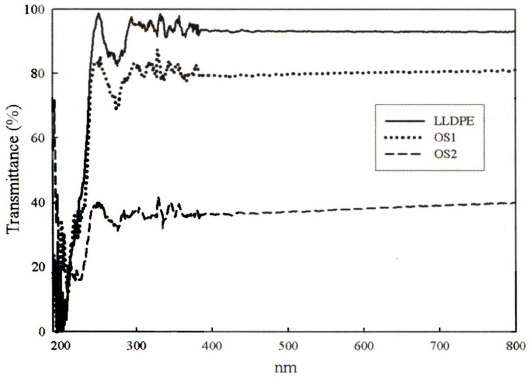


Figure 14. % light transmission of LLDPE, OS1 and OS2

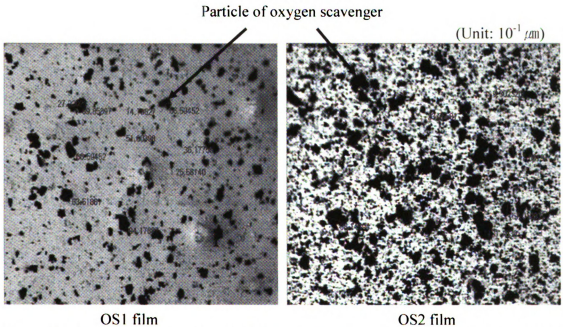


Figure 15. Dispersion state and particle sizes of oxygen scavengers in OS1 and OS2 film

3.3.2. Thermal properties

3.3.2.1. T_g, T_m, and Crystallinity

Using a differential scanning calorimeter (DSC Q 100, TA Instruments, DE), the T_m was determined. The T_m of OS1 was 124.04 ℃, and T_m of OS2 was 123.79 ℃ [Figure 16]. The values of T_m for the two oxygen scavenging films (OS1 and OS2) were nearly the same. The T_g was not measured because it is below the -80 ℃ limit of the system.

As crystallinity generally influences the permeability, the approximate percent crystallinity of OS1 and OS2 can be calculated from measurements of the heat of fusion made using DSC (Selke et al, 2004). The crystallinity of OS1 was 25.6% and for OS2 was 30.8%. The equations for percent crystallinity of OS1 and OS2 are as follows:

$$\text{Percent crystallinity of OS1} = \frac{\Delta Hf1}{\Delta Hf^*} \times 100 = \frac{73.37}{286.2} \times 100 = 25.6\% \quad (3.9)$$

$$\text{Percent crystallinity of OS2} = \frac{\Delta Hf2}{\Delta Hf^*} \times 100 = \frac{88.07}{286.2} \times 100 = 30.8\% \quad (3.10)$$

where, $\Delta Hf1$: Heat of fusion of the sample (OS1)

$\Delta Hf2$: Heat of fusion of the sample (OS2)

ΔHf^* : Heat of fusion of 100% crystalline LLDPE (286.2 J/g)

The value of OS1 (25.6%) in percent crystallinity is lower than OS2 (30.8%). This may be related to decrease mechanical orientation due to the inefficient bubble foam caused by agglomeration in the blown film process.

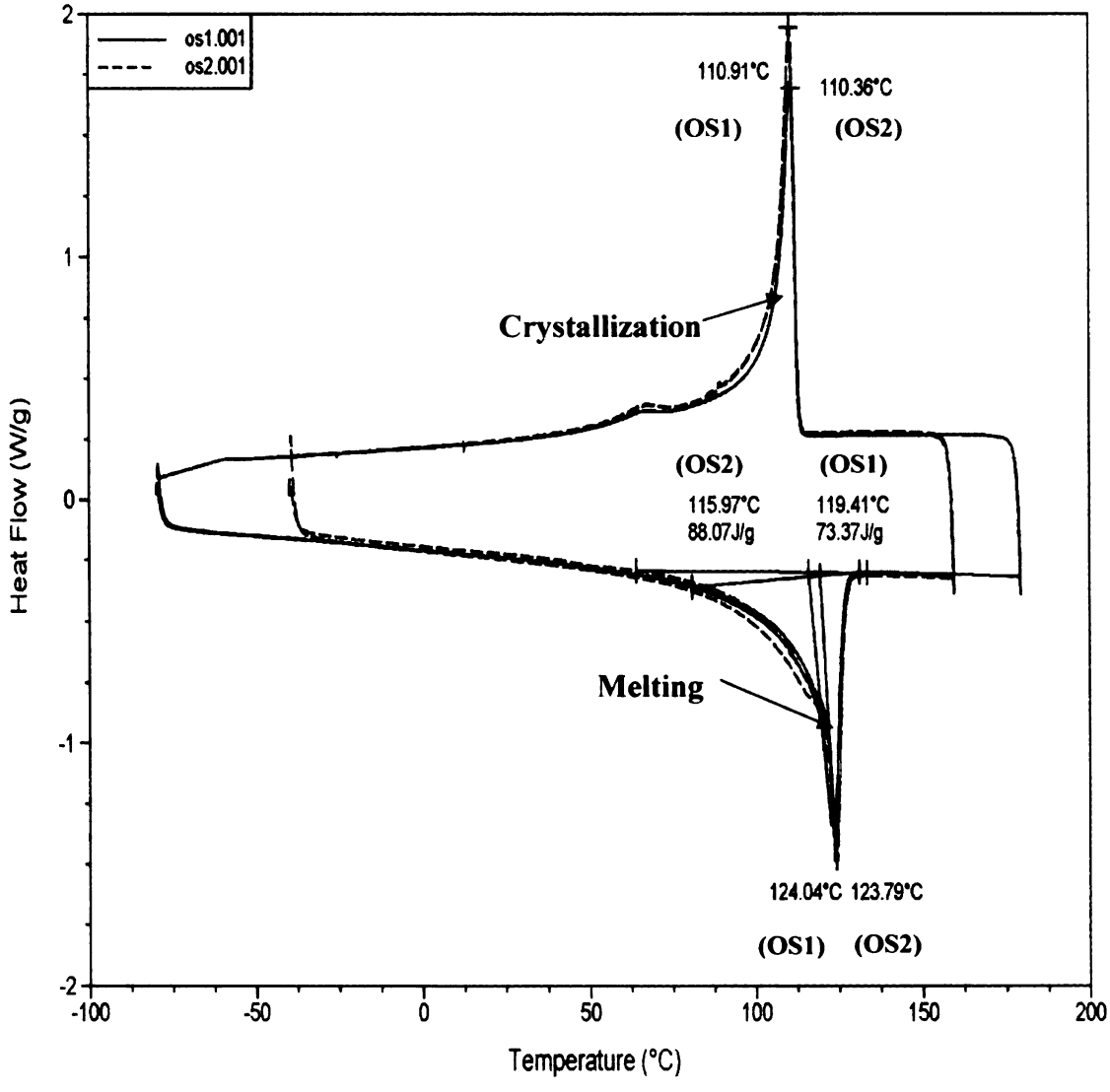


Figure 16. DSC chart of OS1 and OS2

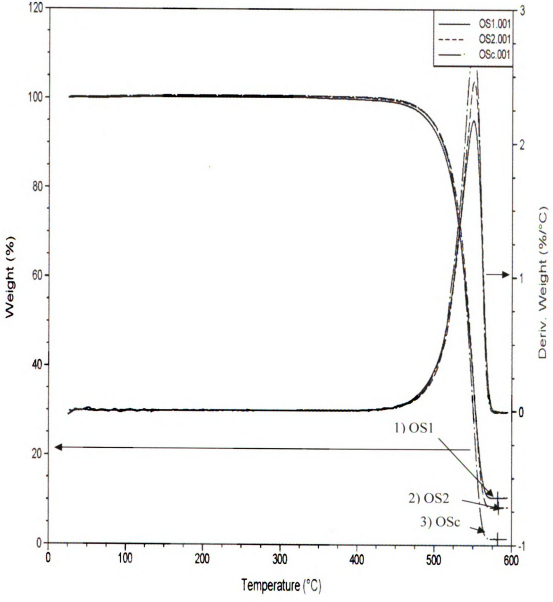
3.3.2.2. Thermo gravimetric analysis (TGA)

From the TGA data in Table 12 and Figure 17, 0.29% by weight of components in OS2 were lost at 444.92 ℃, and at 575.09 ℃ only 8.43% (0.242 mg) remained as residue. The peak gravimetric loss rate was at 530.88 ℃ (2.461 %/℃). The residue of OS1 was

10.63%, but that of the film control was 1.42%. Therefore, the residual materials in the OS1 and OS2 above those of the film control (LLDPE) were about 7 ~ 9%. These major residual materials are assumed to be ferrous components because it is known that the oxygen scavenging compounds consist of about 7 ~ 10 weight percent of iron components in a base polymer such as polyethylene or polypropylene (Brody et al. 2001). The thermal degradation of LLDPE and other additives started in the range of 400 ~ 410 ℃ and was complete at around 570℃. The peak points of gravimetric loss in OS1, OS2 and the control were located in the range of ~545 - 550 ℃ and the rates were ~2.2 - 2.5 %/℃.

Table 12. TGA data for LLDPE, OS1 and OS2

Sample	Gravimetric Loss			Peak Gravimetric Loss			Residue	
	Size (mg)	Temp (℃)	Loss (%)	Temp (℃)	Loss-rate (%/℃)	Temp (℃)	Residue-rate (%)	Residue (mg)
LLDPE	2.90	448.35	0.25	546.24	2.566	571.22	1.422	0.0374
OS1	3.90	406.33	0.23	549.36	2.171	574.28	10.630	0.4145
OS2	2.87	444.92	0.29	550.88	2.461	575.09	8.430	0.2419



1) OS1 residue: 10.63%
2) OS2 residue: 8.43%
3) OSc (LLDPE) residue: 1.422%

Figure 17. TGA chart to compare with LLDPE, OS1 and OS2

3.3.3. Mechanical properties

The tensile strength in the cross direction (CD) and machine direction (MD) of LLDPE films, which was used as a control sample to compare with the films E and F, were 385.91 kg/cm^2 and 379.41 kg/cm^2 respectively, and the break elongation in CD and MD of LLDPE films were 929.7% and 913.9% respectively. Therefore, there were no significant differences between the two directions in LLDPE films ($p \geq 0.05$, $n = 5$). However, the tensile strength in CD and MD of OS1 films decreased to 228.95 kg/cm^2 and 241.80 kg/cm^2 respectively, and the elongation at break in CD and MD of OS1 films also decreased to 700.8% and 612.3% respectively. The differences in these values between LLDPE and OS1 were significant ($p < 0.05$, $n = 5$). For the OS2 film, the values of tensile strength in CD and MD were 262.61 kg/cm^2 and 309.74 kg/cm^2 respectively, and the average elongation at break in CD and MD were 759.2% and 707%, which were also significantly decreased from those of LLDPE films ($p < 0.05$, $n = 5$). Consequently, the decrease of values for OS1 and OS2 may be influenced by the presence of inorganic materials such as ferrous or ferrous oxides in the film. One more interesting thing was that the differences between the values of OS1 and OS2 for MD were significant ($p < 0.05$, $n = 5$). The agglomeration in the OS1 film seemed to affect the decrease of these values. Break strength also showed similar results, as shown in Table 13.

The decrease of values for OS1 and OS2 compared with LLDPE might be influenced by the presence of inorganic materials such as ferrous compounds in the film. The value of OS1 was overall lower than OS2, due to the agglomeration in the OS1 film.

Table 13. Mechanical properties in LLDPE (Control), OS1 (Film E) and OS2 (Film F)

Sample	Film Direction	Tensile Strength (kg/cm^2)	Break Strength (kg/cm^2)	Break Elongation (%)
LLDPE	CD	385.91 ± 26.043 ^{aD}	344.92 ± 26.017 ^{aD}	929.7 ± 36.14 ^{aD}
	MD	379.41 ± 25.237 ^{1D}	339.13 ± 24.327 ^{1D}	913.9 ± 24.89 ^{1D}
OS1	CD	228.95 ± 7.969 ^{bE}	189.91 ± 28.279 ^{bE}	700.8 ± 10.98 ^{bE}
	MD	241.80 ± 12.626 ^{2E}	194.42 ± 12.390 ^{2E}	612.3 ± 11.06 ^{2F}
OS2	CD	262.61 ± 13.355 ^{cE}	219.54 ± 13.291 ^{bE}	759.2 ± 20.27 ^{cG}
	MD	309.74 ± 16.640 ^{3F}	264.13 ± 19.814 ^{3F}	707.3 ± 14.66 ^{3E}

Mean ± standard deviation, n = 5
Different letters or numbers (a through c for CD; 1 through 3 for MD; D through G for between CD & MD) within a column are significantly different ($p < 0.05$)

3.3.4. Oxygen absorbing amount of multi-layer film

The amount of oxygen absorbed was evaluated for OS1 and OS2 multi-layer films incorporated with 20%, 30% and 50% oxygen scavenging (OS) material. From Table 14, the 0 day concentration was calculated as 20.9% oxygen, the same as the oxygen concentration in ambient air. The amount of oxygen in the jar was calculated by multiplying 20.9% by the volume of the jar. The 30 day concentration was measured by oxygen headspace analyzer, and the amount of oxygen was also calculated.

After 30 days at room temperature (23 ℃) and 100% humidity, the oxygen absorption was 5.68 cc/g of film at 50% OS content, 3.36 cc/g at 30% and 2.24% at 20% in the OS1 film. This showed that the oxygen absorption increased at almost the same ratio as the oxygen scavenging content as was expected. The results for the OS2 film

were similar as the average oxygen absorbing amount of OS2 was 6.10 cc/g, but it was significantly different ($p < 0.05$, $n = 3$) from the value for OS1 film. It seemed that the agglomeration of oxygen scavenging material in the OS1 film reduced the amount of oxygen absorbed.

Table 14. Amount of oxygen absorbed

Film	OS content	0 day O_2 amount	30 day O_2 amount	[1] Absorbed O_2 amount	[2] Film weight	[3] **Absorbed O_2 amount /film weight**	[4] O_2 absorb. ratio
		cc/jar	cc/jar	cc	g	cc/g	%
OS1	50%	**201.5**	**178.7**	**22.8**	4.01	**5.68**[a]	50.7
	30%	199.1	189.0	10.1	3.01	3.36	29.9
	20%	205.0	198.3	6.7	2.99	2.24	20.0
OS2	50%	201.9	177.5	24.4	4.00	**6.10**[b]	50.4
	30%	199.3	188.4	10.9	3.00	3.63	30.1
	20%	203.3	196.0	7.3	3.02	2.42	20.0

[1] Absorbed O_2 amount: 30 day O_2 – 0 day O_2 = 201.5 – 178.7 = 22.8 cc
[2] Film weight: The weight of OS film that was inserted in the jar.
[3] **Absorbed O_2 amount/film weight**
[4] O2 absorb. ratio: It is made to evaluate the change of O_2 absorbing ratio to compare with the change of OS content.
- The values of absorbed O_2 amount per film weight in 20% of OS1 or OS2 are considered as 20.0% (O_2 absorb. ratio), the value of absorbed O_2 amount per film weight in 50% of OS1 is calculated as follows:
OS1-50% (5.68)/OS1-20% (2.24) x 20% = 50.7%

Different letters (a through b) within a column in 50% of OS1 and OS2 are significantly different ($p < 0.05$).

3.4. Summary

Development of a multilayer film incorporating iron based oxygen scavenger was done successfully and the OS2 film was preferred to adopt as an oxygen scavenging film to make an active packaging. The conclusion of development of the project can be summarized as follows;

1) Agglomeration in the film

All films except F (OS2) were observed to have various sizes of agglomeration generated during the blown film process, which increased when the content of oxygen scavenger was increased or HDPE resin was used instead of LLDPE resin. Therefore, film F, which was made of OS2 mixed with LLDPE resin and produced by the blown film process at the selected conditions, was preferred to other films based on amount of agglomeration.

2) Optical properties

LLDPE shows the highest value in % light transmission, and the value of OS2 was much lower than OS1. After 400 nm, while LLDPE shows around 95 %, OS1 shows near 80 % but OS2 shows below 40 %. Especially, the value of OS2 was much lower than that of OS1 or LLDPE. It seems that the transparency of OS2 was dramatically reduced due to the good dispersion of oxygen scavenger without any agglomeration and the bigger particle sizes than those of OS1, which can interrupt the light transmission.

3) Thermal and mechanical properties

The value of OS1 (25.6%) in percent crystallinity is lower than OS2 (30.8%). This may be related to decrease mechanical orientation due to the inefficient bubble foam caused by agglomeration in the blown film process. From the TGA analysis, the residual materials in the OS1 and OS2 films were about 7 ~ 9% above the value of residue in

LLDPE. These are assumed to be ferrous components because they are major components in the oxygen scavenger and are not volatilized at 600 ℃.

For the mechanical properties such as tensile & break strength and break elongation, the decrease of value for OS1 and OS2 compared with LLDPE might be influenced by the presence of inorganic materials such as ferrous compounds in the film. The value of OS1 was overall lower than OS2. It might result from lack of uniform thickness in the bubble shape due to agglomerations in the blown film process.

4) Oxygen absorbing amount

The oxygen absorbing amounts of all OS1 and OS2 films increased at almost the same ratio as the oxygen scavenging material contents. Therefore, the oxygen scavenging effects of the films were useful even though it had a multilayer structure containing coextruded LLDPE on the inside of the film. The OS2 film was a little better ($p<0.05$) than that of the OS1, consuming 6.10 cc/O_2 per g film after 30 days storage at room temperature (23 ℃) and 100% RH, because agglomeration in OS1 film resulted in a decrease of oxygen uptake.

3.5. References

Ball G.F.M., *Vitamins in Food: Analysis, Bioavailability, and Stability*, CRC Press, Taylor & Francis Group, Boca Raton, FL, pp. 39-51, 2006.

Barua, A.B. and C.F. Harold, "Properties of retinols," *Molecular Biotechnology*, 10: 167-182, 1998. http://www.springerlink.com/content/b234wu0t1h607182/

Brody, A.L., E.R. Strupinsky, Kline L. R., *Active Packaging for Food Applications*, Technomic Pub., Lancaster, PV, PP. 11-86, 2001.

De Jong, A.R., H. Boumants, T. Slaghek, J. Van Veen, R. Rijk, & M. Van Zandvoort, "Active and intelligent packaging for food: Is it the future?," *Food Additives and Contaminants*, 22: 975-979, 2005.

Foltynowicz, Z., W. Kozak and R. Fiedorow., "Studies of Oxygen Uptake on O2 Scavengers Prepared from Different Iron containing Parent Substances", *Packaging Technology and Science*, 15: 75-81, 2002.

Ozdemir, M. and J.D. Floros, "Active Food Packaging Technologies," *Food Science and Nutrition*, 44: 185-193, 2004.

Selke, Susan. E.M., John D. Culter, Ruben J. Hernandez, *Plastic Packaging*, 2nd Hanser Pub., Munich, pp. 63-72, 2004.

Robertson, G.L., *Food Packaging: Principles and Practice*, 2nd ed., Taylor & Francis/ CRC Press, Boca Raton, FL, pp. 285-311, 2006.

4. DEVELOPMENT OF ACTIVE PACKAGING

4.1. Introduction

In recent times, co-extruded multilayer containers that incorporate ethylene vinyl alcohol (EVOH) or other plastic barrier tubes have been widely used in food, health care and cosmetic packaging. However, EVOH has some limitations for moist products due to its sensitivity to humidity, and plastic barrier materials such as SiO_x or Al_2O_3 coated film also have some limitations at protecting from photo-degradation caused by UV light (Rooney and Yam, 2007). Furthermore, they have critical problems that are the presence of oxygen in the product itself and the residual oxygen of the headspace in the package (Brody at al., 2001). In particular, it is extremely difficult to control or remove the oxygen in the headspace by nitrogen gas flushing during a finishing process such as tube-sealing in the cosmetics industry.

The oxygen in the headspace of the packaging and in the product itself or transmitted light can cause not only reduction of retinol content, but also off-flavor, color change, and increased microbial growth (Ball, 2006; Barua and Harold, 1998). For these reasons, packaging containing aluminum foil was designed, instead of plastic barrier materials, to protect perfectly from the sunlight and the outside oxygen. Additionally, as active packaging, a ferrous based oxygen scavenger material that is incorporated into the core-layer of a three-layer blown film was contrived to solve the problem in conventional co-extruded multi-layer barrier containers or other passive packaging through absorbing the oxygen inside the packaging [Figure 18]. Thus, the first objectives of this study are:

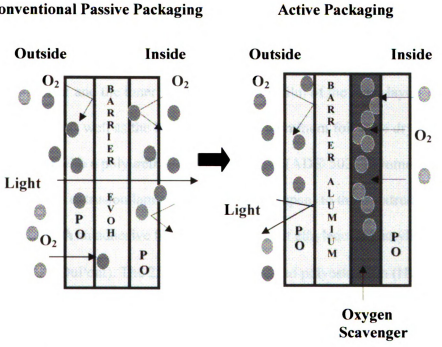
1) Development of an oxygen scavenging film

- To set up a proper multilayer structure and process conditions

- To have the best value for mechanical, optical and thermal properties

2) Development of an active package for cosmetics

- To evaluate the performance of the oxygen scavenger in reducing oxygen concentration in the headspace of active packages, compared with conventional packages
- To evaluate extension of shelf life through the evaluation of retinol content in cosmetics.



EVOH: Ethylene Vinyl Alcohol
PO: Polyolefins group

Figure 18. Design of active packaging for cosmetics

4.2. Materials and methods

4.2.1. Package design

Figure 19 shows the structure of the package designed for this project. In order to perfectly protect against degradation of retinol components by light and oxygen from outside conditions and keep moisture in the inside of the package for activation of the oxygen scavenger, 16 ㎛ thickness of aluminum foil was used as a barrier material in the active packaging system. The OS2 film was selected for the active component, because it did not have any agglomerations, so it was expected to have better printability, mechanical properties and oxygen scavenging capacity. For good sealing, a mono-layer LLDPE film, thickness 30 ㎛, made by a blown extrusion film line, was co-extruded on both the outer layer and the inner layer. The LLDPE film of the outer layer and the adjacent PET film as well as the PET film and the aluminum foil were dry laminated (Okazaki, Japan) with a polyurethane based adhesive (AD® 502, Toyomorton). The aluminum foil was extrusion laminated (Sumitomo, Japan) to the coextruded oxygen scavenger film with an adhesive that is a copolymer of ethylene and acrylic acid (Nucrel® 30707, DuPont). The 25 ㎛ biaxially oriented polyester film (Hyosung, Korea) was used to obtain the desired stiffness. The design of the active packaging and laminated structure can be found in the patent for "laminate for cosmetic tube with oxygen absorbing function" (Shin, et al., 2006).

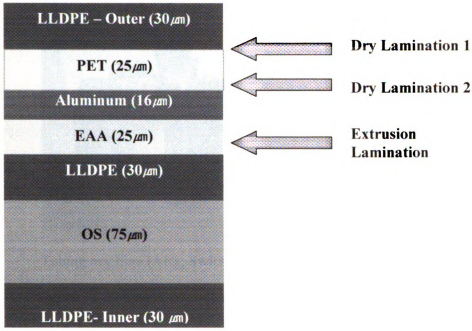
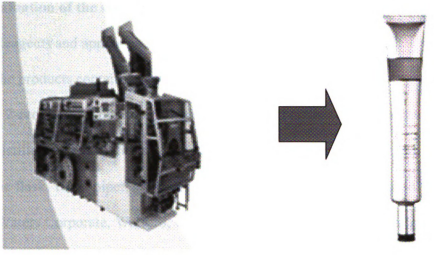


Figure 19. Desired structure of active packaging and lamination processes

4.2.2. Tube production

The roll of active packaging in Figure 20 was printed with a 6 color offset printer (Komori, Japan) using UV inks (Toyo Ink, Japan). The second step was to make a tube by folding the roll and sealing the seam area, and then the mouth part was inserted into the tube and sealed. The next step was an external coating with 150 to 200 ㎛ of polyethylene on the 'LLDPE-Outer' layer in Figure 18. Then finally a closure was attached to the tube in the customer's packaging line.



Tubing machine (Aisa, Switzerland) Final product

Figure 20. Tubing & over-coating process

4.2.3. Evaluation for residual oxygen in the headspace of packaged products

The trends in reduction of oxygen concentrations in the headspace of packages that were filled with real cosmetic products were measured as an evaluation method for performance of the oxygen scavenger. The oxygen concentration was measured at the tail of the tube, and samples were withdrawn at a rate of 40 ml/min, and then passed by the oxygen sensor using an Oxygen Headspace Analyzer Model-3500 (Illinois Instruments). Two kinds of packages were evaluated. One was a package that was laminated with the OS2 film, the other sample (control sample) was made of LLDPE mono-layer film instead of the oxygen scavenging film (OS2). Samples were all stored in a chamber at 23 ℃, 65 % RH. Tests were performed at 7, 30, 60, 90, 120, 150 and 180 days after filling with real cosmetic products.

4.2.4. Evaluation of the shelf life of retinol in products

4.2.4.1. Reagents and apparatus

The products containing retinol were supplied by Amore Pacific. Standard retinol (99.0 %), 2-propanol, dimethylformamide (DMF), and methanol were obtained from Sigma. Distilled water used was HPLC grade from J.T. Baker. A 100 ml amber volumetric flask, 10 ml pipet, sonicator and magnetic stirrer were also used. An HPLC system (Waters Corporate, Watford, UK) consisting of a separation module (Waters 2695) with UV detector (Waters 2487), C18 column with inside dimensions of 150 x 5 mm (Waters) and 0.45 ㎛ micro-filter (Fisher Scientific, PA), were used for analysis of the sample solutions.

4.2.4.2. Sample handling

As retinol is easily degraded by sunlight, heat and oxygen, all handling and experimental procedures were carried out away from direct sunlight, and samples were stored at under 4℃ in a refrigerator. All experiments were replicated five times.

4.2.4.3. Calibration of standard solution

Stock solutions of standard retinol were prepared by dissolving 10 mg in 100 ml of 2-propanol in an amber volumetric flask. Working standard solutions were prepared by dissolving each volume (1, 4, 10 and 30 ml) from the stock solution in 100 ml of 2-propanol as the 1^{st}, 2^{nd}, 3^{rd} and 4^{th} working standard solutions. Using the 2^{nd} working standard solution, the exact concentration was determined spectrophotometrically (UV/VIS Spectrometer from Perkin Elmer, Wellesley, MA) at 325 nm. After testing the four working standard solutions by HPLC, the standard calibration curve was constructed

by calculating the area response (AU) of the peak [Figure 21] for each working standard solution (mg/100ml). The standard curve is shown in Figure 22.

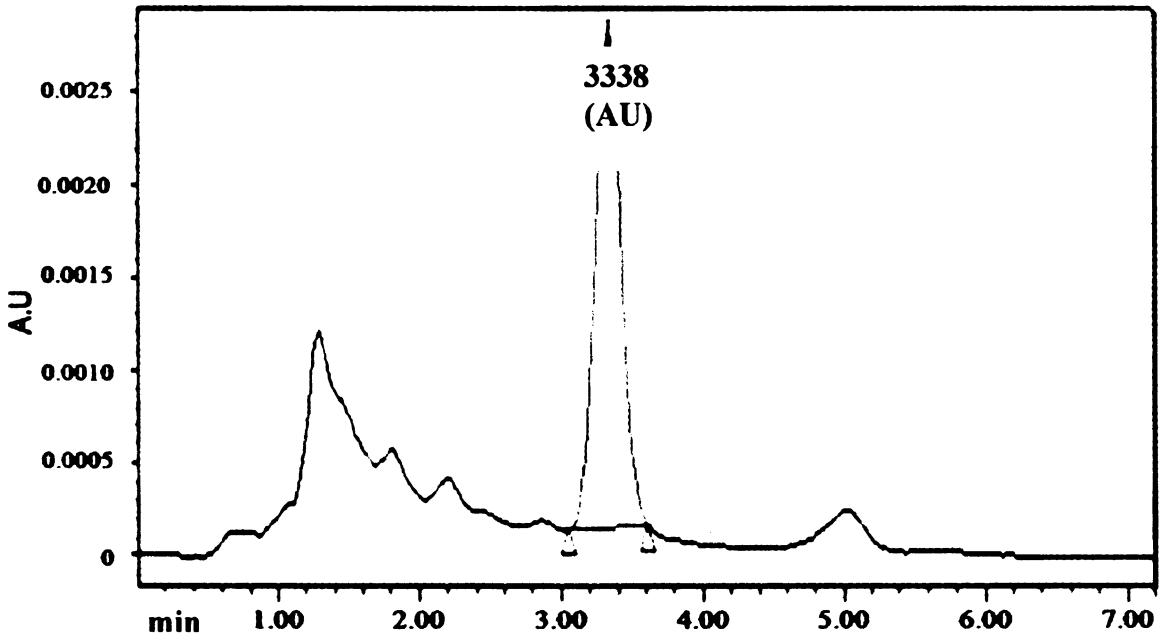


Figure 21. The area response in peak of a working standard solution of retinol in HPLC

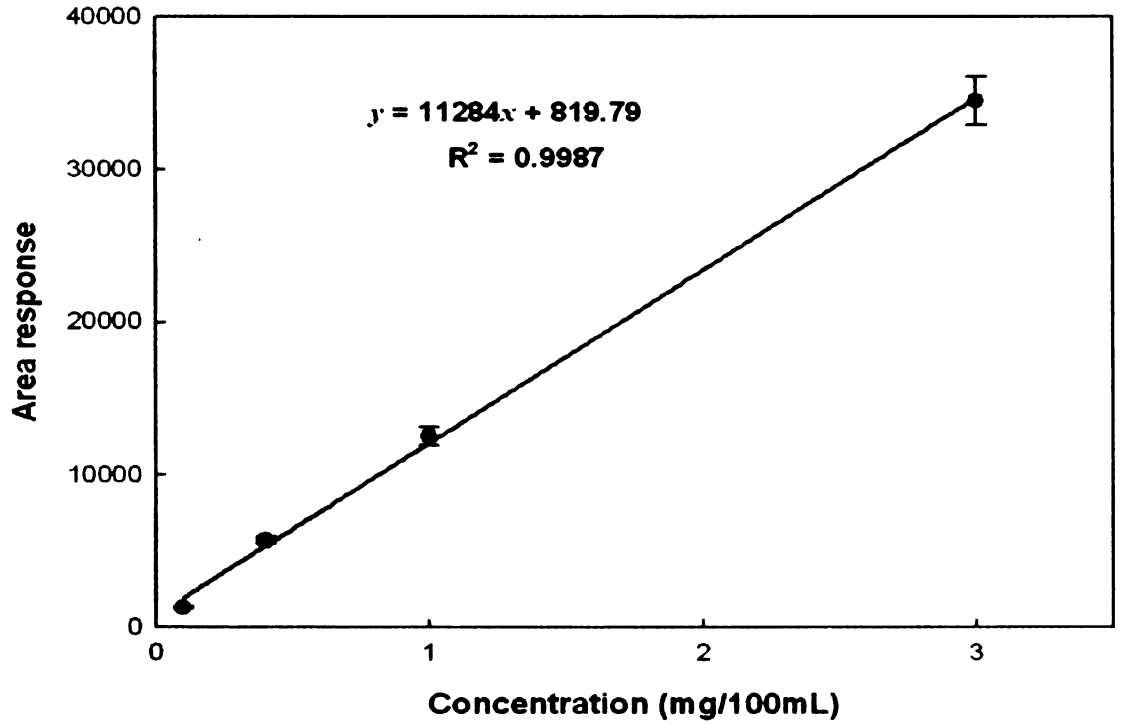


Figure 22. Standard calibration curve of retinol in HPLC

4.2.4.4. Sample extraction

Stock solutions of real products (samples) containing retinol were prepared by dissolving approximately 2 g in 20 ml of dimethylformamide (DMF) in an amber 100 ml volumetric flask, because DMF is very useful for dissolving cream products that contain lots of oil or wax mixed with retinol. After dissolving the stock solutions for 10 minutes with a sonicator, a working solution was prepared by dilution to 100 ml with HPLC grade methanol, and mixing by magnetic stirrer for 30 minutes. The sample solutions were all prepared to inject into empty amber glass bottles using a 0.4 μm syringe filter.

4.2.4.5. Calculation for content of retinol in sample solutions

Retinol in the sample solutions was analyzed using a Waters' HPLC system. The mobile-phase solution was methanol and distilled water (93:7), with injection volume 10 $\mu\ell$, and flow rate 1.0 ml/min. The retinol concentration was determined using a UV detector at 325 nm. The content of retinol in sample solutions was determined by the following equation:

$$\text{Content of retinol (IU/g)} = \frac{Cst \times 3333(IU/mg)}{Csa} = \frac{\frac{(Rs - 819.79)}{11284} \times 3333}{2} \quad (4.1)$$

where Cst = retinol concentration of standard solution (mg/100ml)

Csa = retinol concentration of sample solution (g/100ml)

Rs = response area for the sample (area unit: AU)

1 mg retinol = 3333 IU, 1 IU = 0.300 μg

4.2.5. Statistical Analysis

Statistical evaluation of the data was performed using SPSS (SPSS Inc., 2004). Significance levels were reported at the 95 % confidence level ($p < 0.05$) using Tukey's honestly significant difference (HSD) multiple comparison. The results of statistical analysis are shown as mean values $\pm$ standard deviation.

4.3. Results and discussions

4.3.1. Oxygen concentration in the headspace of packaged products

Figure 23 shows the trend of oxygen concentration in the headspace of packages filled with a real cosmetic product during 180 days at room temperature. The conventional packaging samples (Control: LLDPE) consisted of packages laminated with linear low density polyethylene monolayer films, and active packaging samples (Active: OS) were made of packages laminated with the film F that contained oxygen scavenger. While the average oxygen concentration in the headspace of OS was rapidly reduced to 3.42 % at 7 days and reached 0.00 % within 30 days, that of LLDPE had a much higher level of over 12.58 % at 30 days and 9.50 % at 150 days. Furthermore, the value of OS continued to be at 0.00 % to 120 days and was only 0.01 % at 150 days. This means that OS was effective in oxygen scavenging. Table 15 shows the oxygen concentration data for LLDPE and OS and results of statistical analysis.

Table 15. Trends of oxygen concentration in headspace of both control and active samples (stored at 23 ℃, 65 % RH)

Sample		0 day	7 day	30 day	60 day	90 day	120 day	150 day	180 day
LLDPE	Avg	20.07	16.68	12.58	10.63	10.07	9.79	9.50	9.29
(Control)	Std	0.125	0.374	0.589	0.423	0.342	0.325	0.275	0.235
	Dev	a 1	a 2	a 3	a 4	a 4,5	a 4,5	a 5	a 5
OS	Avg	20.12	3.42	0.00	0.00	0.00	0.00	0.01	0.01
(Active)	Std	0.120	0.540	0.000	0.000	0.000	0.000	0.012	0.010
	Dev	a 1	b 6	b 7	b 7	b 7	b 7	b 7	b 7

Different letters (a through b) within a column are significantly different ($p < 0.05$).
Different letters (1 through 5) within a row are significantly different ($p < 0.05$). $n = 3$

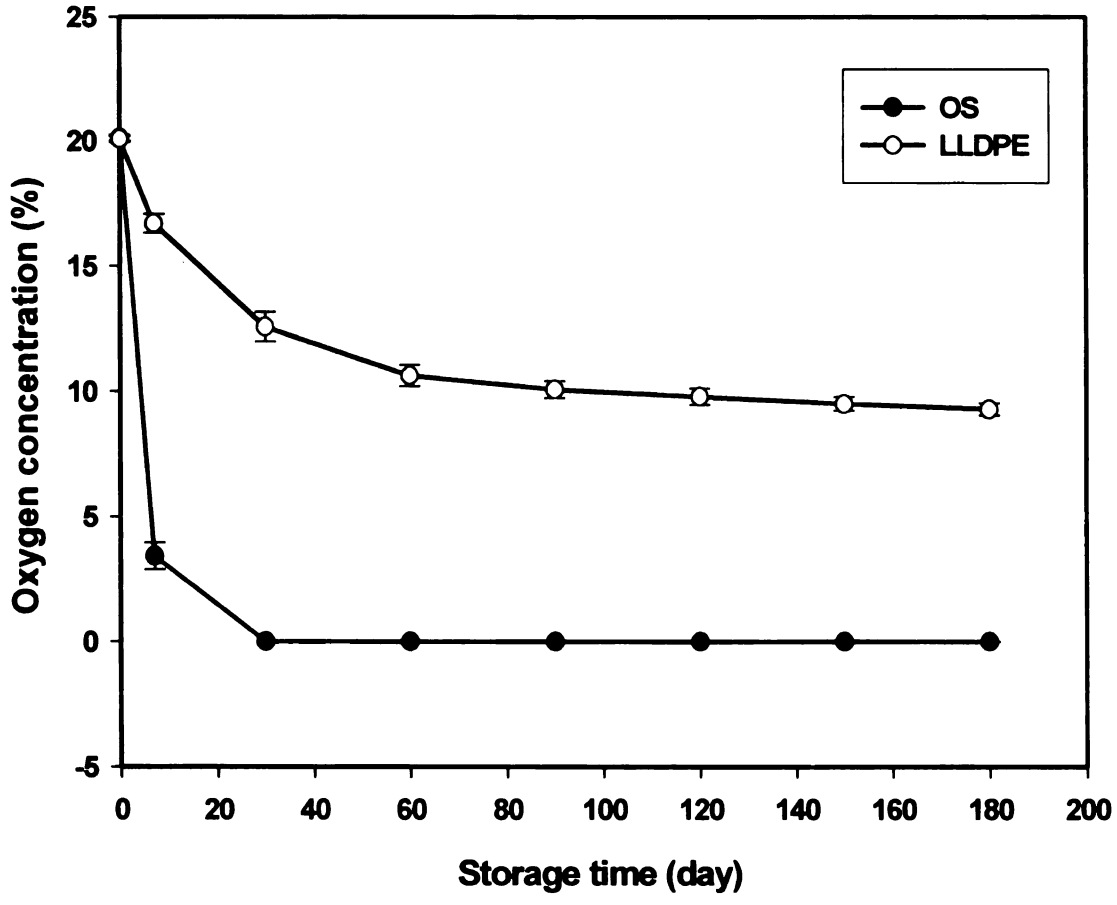


Figure 23. Oxygen concentration trends in headspace (stored at 23 ℃, 65 % RH); OS was rapidly reduced to 3.42 % at 7 days and reached 0.00 % within 30 days, but LLDPE had a much higher level of over 12.58 % at 30 days and 9.50 % at 150 days.

4.3.2. Shelf life of retinol in packaged products

For determination of the shelf life of real products containing retinol, active packages were compared with conventional packages under the same conditions as control samples. Figure 24 shows the trends of retinol content in cosmetics in both conventional packages (Control: LLDPE) and active packages (Active: OS) which were stored for 1, 2, 4, 8, 12 and 24 weeks at room temperature.

From Table 16, it can be seen that there were no significant differences between the LLDPE and OS samples in the first and second week ($p < 0.05$, $n = 3$). However, at

four weeks, the difference between the two samples was significant ($p < 0.05$, $n = 3$). Moreover, at 24 weeks, the difference between the LLDPE and OS sample was over 500 IU. Furthermore, the average value in OS of 3,019 IU at 24 weeks was more than that of the LLDPE sample at 12 weeks. Therefore, it can be concluded that the shelf life of retinol in the cosmetic was significantly extended by the active package.

As it mentioned in the section of 1.3., retinol is a group of fat-soluble compounds that has an unstable structure consisting of a β-ionone ring, a conjugated isoprenoid side chain and a polar terminal group (-OH). Therefore, it is readily oxidized or isomerized to altered compounds, especially in the presence of oxidants including air, and influences such as light and heat. It is labile toward active components such as silica, strong acids and solvents that have dissolved oxygen or peroxides (Ball, 2006; EGVM, 2003; Barua and Harold, 1998).

From Figures 22 and 23, in spite of the fact that oxygen concentration in the OS tube was maintained at 0.0% from 30 days to 180 days after 30 days, the retinol content was still decreased. It seems that retinol was degraded not only by oxygen, but also by acids in cosmetics additives, which can cause rearrangement of the double bonds and dehydration. Silica, which is in direct contact with retinol, in additives of cosmetics or in the inner layer of the OS tube and long storage conditions (6 months) at room temperature (23 ℃) also seems to cause the loss of retinol.

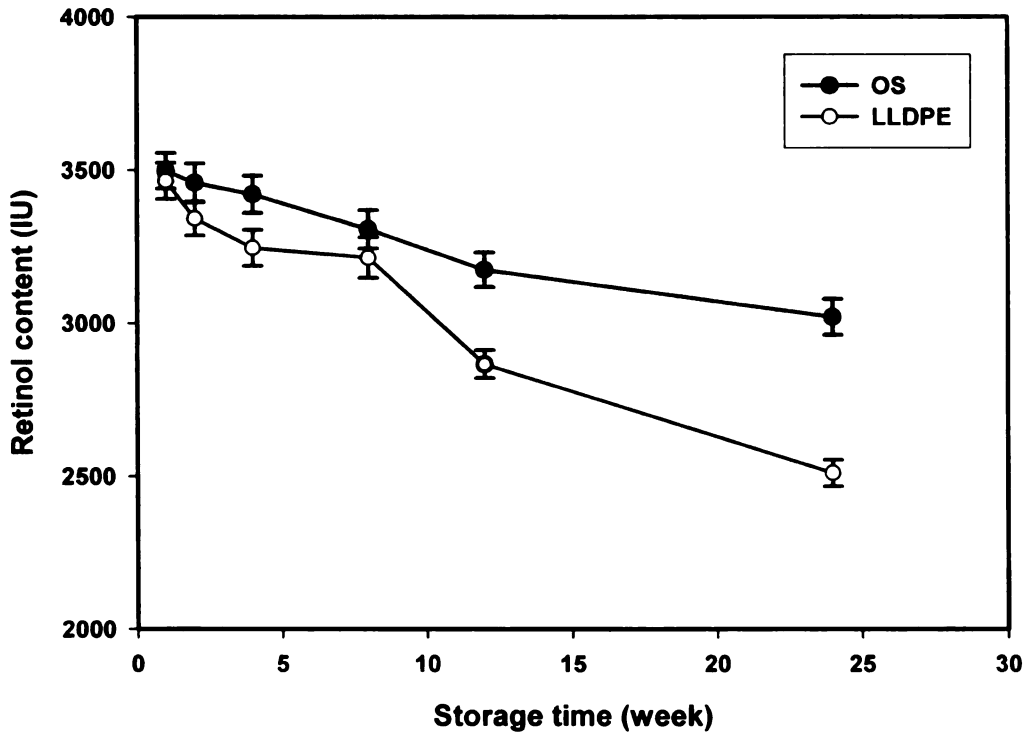


Figure 24. Trends for the loss of retinol content in cosmetics;
the difference between the LLDPE and OS sample was over 500 IU at 24 weeks.

Table 16. Retinol contents vs. storage time FOR the conventional (Control) and active package (OS) samples. The structure of Control was LLDPE/PET/AL/LLDPE, and OS was LLDPE /PET/AL/LLDPE +OS + LLDPE.

Sample	1 week	2 weeks	4 weeks	8 weeks	12 weeks	24 weeks
LLDPE (Control)	3,464 ± 60 a 1,2	3,341 ± 56 a 1,2,3	3,245 ± 59 a 3	3,213 ± 66 a 3	2,866 ± 46 a 5	2,511 ± 43 a 6
OS (Active)	3,498 ± 58 a 1	3,458 ± 64 a 1,2	3,420 ± 60 b 1,2	3,306 ± 63 a 2,3	3,173 ± 56 b 3,4	3,019 ± 59 b 4,5

Mean ± standard deviation, n = 3, Unit : IU
Different letters (a through b) within a column are significantly different ($p < 0.05$).
Different letters (1 through 6) within a row are significantly different ($p < 0.05$).

4.3.3. Estimation of the extended shelf life of retinol in packaged products

To determine the effects of the extended shelf life of an active packaging using oxygen scavenger, the trend line equation and R^2 value was calculated using Micro Excel of MS Office 2004 program. Among the six types of trend lines (linear, logarithmic, polynomial, power, exponential and moving average), the power equation was selected as the best model. The best fit equations and corresponding R^2 value of the LLDPE and OS samples are shown in Figure 25.

The end of shelf life is considered a retinol concentration of 2,500 IU. According to the regulations of the FDA in Korea for functional cosmetics such as retinol cream, the retinol cream should contain more than 90.0 % of the listed content of the retinol ($C_{20}H_{30}O$) as a major component, and the standard for a retinol cream by the Korean FDA (2007-44) is 2,500 IU.

Therefore, the expiration data of the product in a conventional package (LLDPE) is less than 6 months. The calculated time to reach 2,500 IU using the OS package is 51.6 weeks (361 days), using the following equations:

$$y = 3496\, e^{-0.0065\, x} \text{, and } y = 2{,}500 \text{ IU} \qquad (4.2)$$

$$x = \frac{\ln\left(\frac{2500}{3496}\right)}{-0.0065} = 51.6 weeks \qquad (4.3)$$

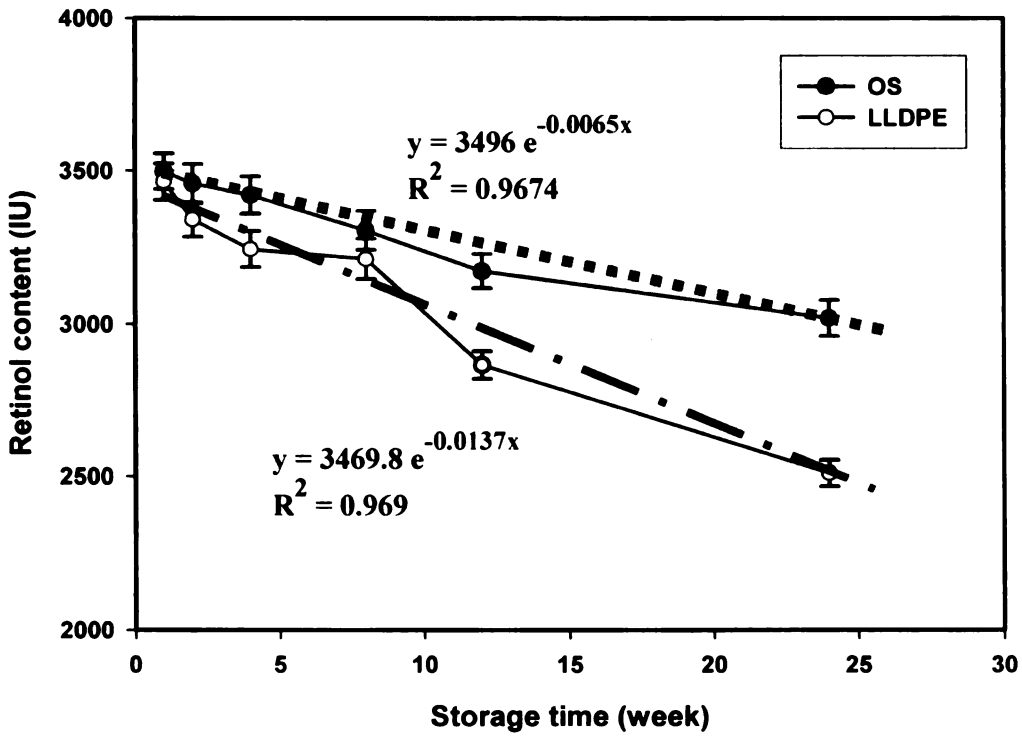


Figure 25. Trend line of the retinol content in cosmetics (stored at 23 ℃, 65% RH)

4.4. Summary

Development and evaluation of the active packaging for cosmetics was done successfully. While development of an active packaging was executed by converting processes such as dry and extrusion laminating, evaluation was carried out through an analysis for the oxygen concentration in the headspace of packaged products and evaluation of the shelf life for retinol in the cosmetic. The conclusion of development of the project can be summarized as follows;

1) Oxygen concentration in the headspace of packaged products

Oxygen in active packages was rapidly reduced compared to conventional packaging, reaching 0.0% from the original 20.9% within 30 days when stored at 23 ℃ and 65% RH, while the value in conventional packages still remained near 10.0% after 180 days.

2) Shelf life of retinol in cosmetics

While the retinol contents in conventional packages were rapidly reduced from 3,464 IU to 2,511 IU after 24 weeks when stored at 23 ℃ and 65 % RH, the value in active packages reminded over 3,000 IU after 24 weeks. The percentage loss of retinol was only 16.1 % after 24 weeks in active packages, but it was almost 2 times as much 30.3% after 24 weeks to compare with initial content (0 week) in conventional packages. A shelf life of 51.6 weeks is estimated, based on reduction of retinol to 2,500 IU.

4.5. References

Amore Pacific Corp., "Test method of retinol in product," in test method (APTM 0189) of R&D Center, 2006.

Ball G.F.M., *Vitamins in Food: Analysis, Bioavailability, and Stability*, CRC Press, Taylor & Francis Group, Boca Raton, FL, pp. 39-51, 2006.

Barua, A.B. and C.F. Harold, "Properties of retinols," *Molecular Biotechnology*, 10: 167-182, 1998. http://www.springerlink.com/content/b234wu0t1h607182/

Brody, A.L., E.R. Strupinsky, Kline L. R., *Active Packaging for Food Applications*, Technomic Pub., Lancaster, PV, pp. 48-75, 2001.

EGVM (Expert Group on Vitamins and Minerals), "Safe Upper Levels for Vitamins and Minerals," Food Standards Agency (FSA), UK, PP. 110-126, May 2003. http://www.food.gov.uk/multimedia/pdfs/evm_a.pdf

Shin, Y.J., M.I. Kim and J.Y. Kim, "laminate for cosmetics tube with oxygen absorption function," Korean Application Number: 20-2006-0004013, 2006.

Rooney, M. L., and K. L. Yam, "Novel Food Packaging," in J. Smith, 2nd ed., *Technology of Reduced Additive Foods*, Blackwell Pub., Oxyford, UK, pp. 61-83, 2007.

5. RESEARCH FOR THE MIGRATION BEHAVIOR OF OXYGEN SCAVENGER IN ACTIVE PACKAGING

5.1. Introduction

Consumers require to be assured that packaging is fulfilling its function of protecting the integrity, freshness and safety of products. To guarantee and improve the performance of the packaging, innovative active packaging concepts are being successfully introduced and applied in the USA and Japan. However, in Europe, the development and application of active packaging systems have been limited because of legislative restrictions and fear of consumer resistance (De Kruijf et al., 2002). In other countries such as Korea, there are not any regulations for these concepts and there is a lack of knowledge about consumer acceptance of the systems. Furthermore, despite the food or cosmetics industries' concerns about whether the active ingredients migrating from packages might be harmful, there are no regulations to limit their development.

The key regulatory issue is food-contact approval. It is often required because active packaging may affect foods in two ways. Active packaging substances may migrate into the food or may be removed from it. Migrants may be intended or unintended. Intended migrants include antioxidants, ethanol and antimicrobial preservatives which require regulatory approval in terms of their identity, concentration and possible toxicology effects. Unintended migrants include various metal compounds, such as iron based oxygen scavengers, that could enter foods. Food additive regulations require identification and quantification of any such unintended migration (Day, 2003). However, no specific regulations exist on testing the suitability of active packaging systems in direct contact with foods and, in many cases, the testing protocols used are not

necessarily appropriate, being based on those developed for plastic packaging materials (Robertson, 2006).

Currently, the most widely used active packaging system is probably the oxygen absorber (Smith et al., 1995). This may be used in sachets, as adhesive labels, incorporated in packaging such as film, trays or other forms (Teumac, 1995: Brody et al., 2001). Sachets containing active substances are often in contact with packaged foods, giving rise to the possibility that their migration into the foodstuff might be significant, especially in the case of moist, fatty and/or acid foodstuffs (Ahvenainen and Hurme, 1997). Although there are many research papers that have been published on the migration of plastic monomers and/or additives into foods or alternative food simulants (e.g. Alnafouri and Franze 1999; O'Brien et al., 1999; Gilbert et al., 2000; O'Brien and Cooper 2001; Riquet et al., 2001), there is only a small amount of literature on the determination of migration from active packaging (Lopez-Cervantes et al., 2003). Furthermore, it is even more lacking in the cosmetics and medical fields. Thus, the second objectives of this work are:

1) To investigate the migration behavior of the oxygen scavenger incorporated in the middle layer of multilayer film, which is not in direct contact with the food simulants in active packaging [Figure 26].

2) To quantify migration into a variety of alternative simulants.

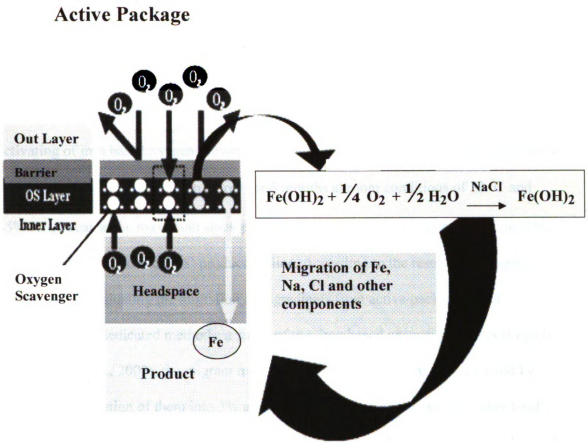


Figure 26. Migration from active packaging to cosmetics

5.2. Materials and methods

5.2.1. Migration components and behaviors

5.2.1.1. Materials

To investigate the various migration components and behaviors resulting from activating of iron based oxygen scavengers, three samples were selected. The first sample was the OS film which had been stored for 6 months at room conditions of 23 ℃ and 65% RH, because the maximum stock period for empty packages is generally 6 months before filling on the customers' production line. According to the research by Lopez-Cervantes for evaluating the migration of ingredients from active packaging and development of dedicated methods: a study of two iron based oxygen absorbers (Lopez-Cervantes J. et al., 2003), the migrant main elements were identified as Na, Cl and Fe, and overall migration of them into 3% acetic acid was greater than into any other food simulants such as 95% ethanol, olive oil and distilled water. Therefore, the second sample was selected from the OS film after migration test with 3% acetic acid, which was stored for 10 days at 40 ℃ after 6 months passed in room conditions of 23 ℃ and 65% RH. Finally, an active package filled with real cosmetics, retinol cream, was selected after 6 months storage at room conditions after filling.

5.2.1.2. Sample preparation

All specimens were cut on the cross-section by Microtome (Model RMC Power Tome XL, Boeckeler Instruments Inc., Tucson, AZ) [Figure 27-1] for SEM & EDS analysis. The cutting operation was done by flushing liquid N_2 gas at - 120 ℃, and the operating temperature of the knife was - 55 ℃. A glass type knife was used for cutting the tube and a diamond knife was used for the film. All cutting speeds were 0.7 mm/sec.

After microtoming, the surface of the samples was coated with carbon-sputter by a Carbon Coater (Model EFFA MkII, Ernest F Fullam Inc., Latham, NY) [Figure 27-2]. This was used instead of the gold coating method that is generally used in analysis of polymer, because the samples contained metal components in oxygen scavenger and gold would make the analysis difficult by absorbing a high percentage of the X-rays produced and adding strong X-ray peaks to the spectrum.

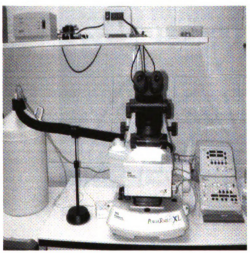


Figure 27-1. Microtome

Figure 27-2. Carbon Coater

5.2.1.3. SEM & EDS analysis

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) microanalysis was used to analyze the main components of the oxygen scavenger in the specimens and observe migrant behavior in the inner layer which is in direct contact with the food simulants or cosmetic, adjacent to the core layer in the specimens, after 6 months at room temperature. The SEM was model JSM - 6400 (JEOL, Japan) configured with a lanthium hexaboride (LaB6) filament, and INCA X-sight 6506 (Oxford, England) [Figure 28]. To get the best image SEM, Snapshot 3 was used, preconfigured to collect a

4096 x 3072 pixel image with a 50 μs pixel dwell time. The acceleration voltage was15 kV and vacuum was 10^{-7} Torr. For EDS, the Analyzer Mode-quantitation was used with an accelerating voltage of 20 Kv.

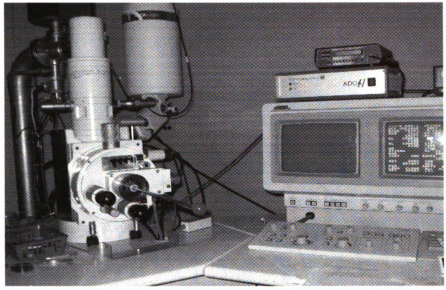


Figure 28. SEM & EDS

5.2.1.4. Identification of the main elements of oxygen scavenger

Figure 29 and Figure 31 show a particle of oxygen scavenger in the cross section of OS1 and OS2 film, which were laminated in packages that had been stored for 6 months at room conditions (23 ℃ and 65% RH) after filling with real product. From the sites of 'Spectrum 1' in the two figures, carbon (C), oxygen (O) iron (Fe), sodium (Na), chloride (Cl), phosphorus (P), silica (Si) and potassium (K) were revealed [Figure 30 and 32-1]. To clarify the main elements, several analyses were executed, and calcium was revealed additionally on the site 'Spectrum 2' in OS2 film [Figure 33-2].

Si was present in both OS1 and OS2 but in very small amounts as impurities and

was also detected in LLDPE film without oxygen scavenger [Figure 33, 34-1 and 34-2]. P was present only in OS1, and Ca was present only in OS2 [Figure 32-2]. Therefore, Fe, Na and Cl, in addition to C and O, are the main elements in these oxygen scavengers.

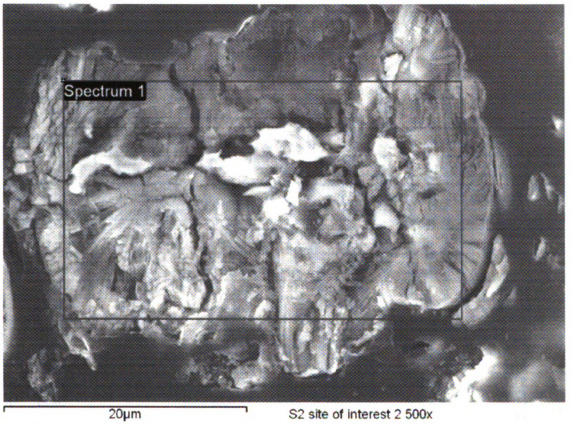
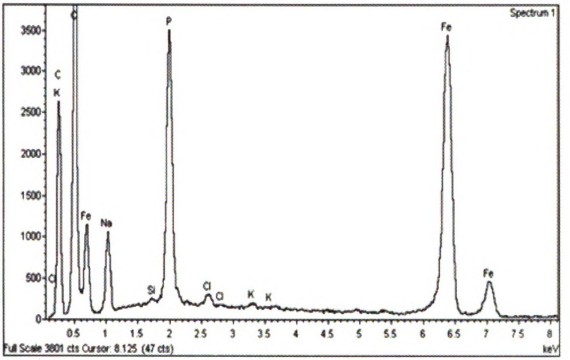


Figure 29. Appearance of a particle of oxygen scavenger in OS1 film



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	56.38	0.5244	35.66	0.44	50.86
O K	67.80	0.6462	34.78	0.33	37.24
Na K	5.37	0.5695	3.12	0.08	2.33
Si K	0.18	0.7841	0.08	0.02	0.05
P K	20.32	1.1957	5.64	0.07	3.12
Cl K	0.60	0.7772	0.26	0.03	0.12
K K	0.32	1.0487	0.10	0.02	0.04
Fe K	51.00	0.8309	20.36	0.20	6.24
Total			100.00		

Figure 30. All elements analysis on the site of Spectrum 1 in OS1 film

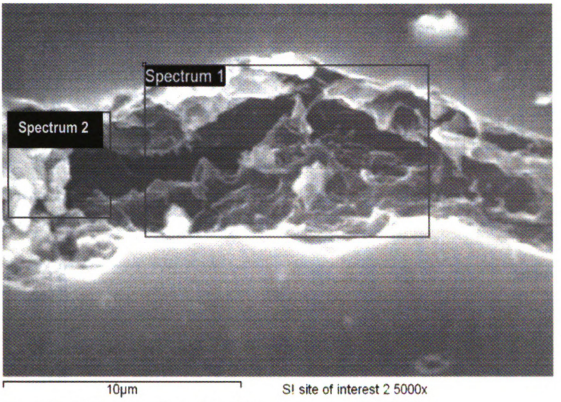


Figure 31. Appearance of a particle of oxygen scavenger in OS2 film

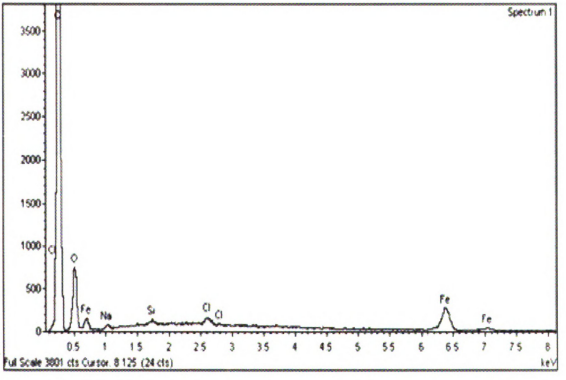
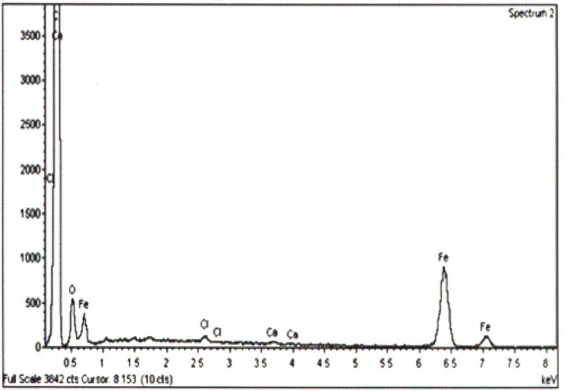


Figure 32-1. All elements analysis on the site of Spectrum 1 in OS2 film

Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	29.65	1.2621	71.04	0.49	78.55
O K	29.23	0.3639	24.29	0.50	20.17
Na K	0.69	0.7534	0.28	0.05	0.16
Si K	0.39	0.9042	0.13	0.04	0.06
Cl K	0.90	0.8301	0.33	0.04	0.12
Fe K	10.20	0.7847	3.93	0.13	0.94
Total			100.00		

Figure 32-1. *(Continued)*



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	35.47	1.3744	81.82	0.34	89.81
O K	9.86	0.3131	9.99	0.34	8.23
Cl K	0.40	0.8355	0.15	0.02	0.06
Ca K	0.32	0.9986	0.10	0.02	0.03
Fe K	19.71	0.7873	7.94	0.12	1.87
Total			100.00		

Figure 32-2. All elements analysis on the site of Spectrum 2 in OS2 film

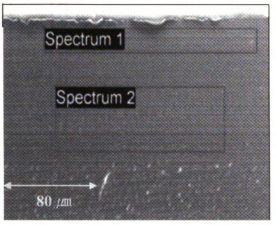
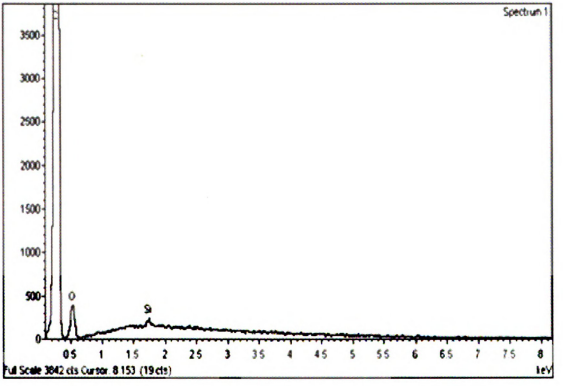
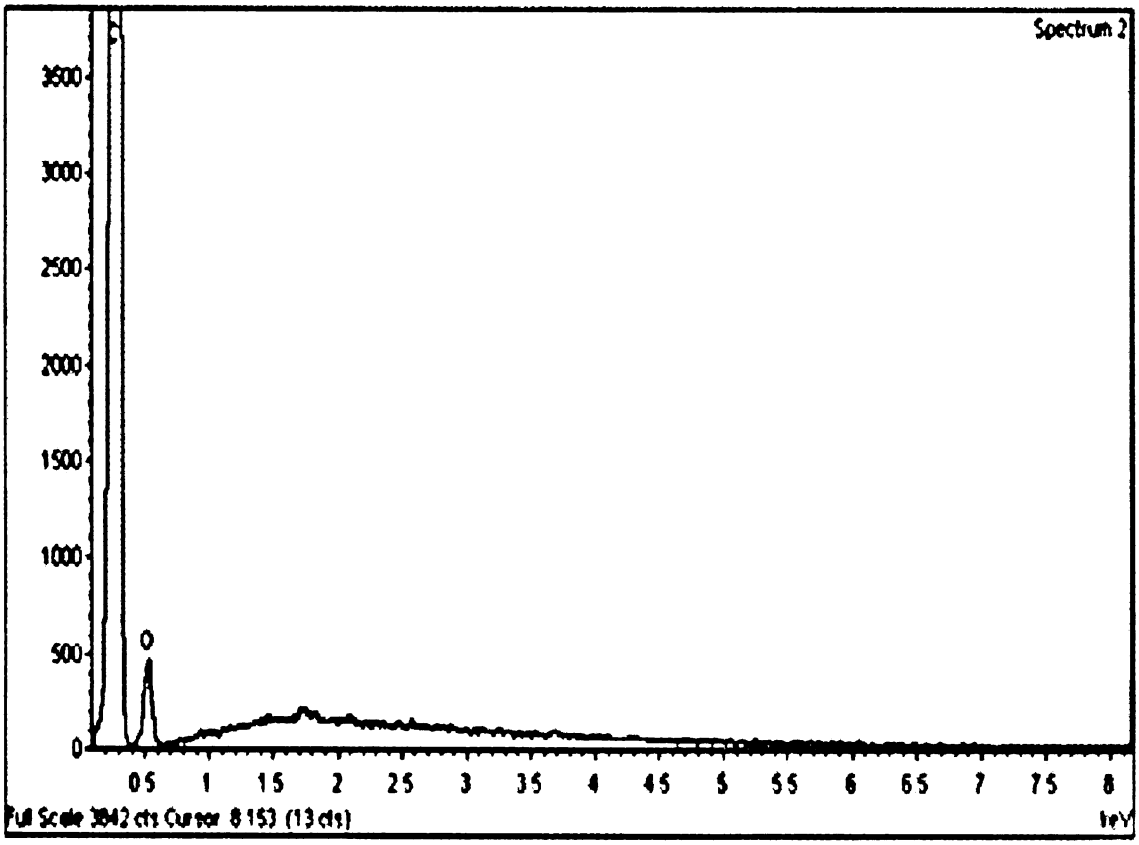


Figure 33. Spectrum sites of LLDPE film



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	49.39	1.8499	90.43	0.35	92.69
O K	7.63	0.2747	9.41	0.35	7.24
Si K	0.44	0.9728	0.15	0.02	0.07
Total			100.00		

Figure 34-1. All elements analysis on the site of Spectrum 1 in LLDPE film



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	52.00	1.8747	90.20	0.34	92.46
O K	8.31	0.2758	9.80	0.34	7.54
Total			100.00		

Figure 34-2. All elements analysis on the site of Spectrum 2 in LLDPE film

5.2.2. Quantitative analysis of migration

5.2.2.1. Film samples

Experiments were carried out using LLDPE, OS1 and OS2 films having three layer structures produced by co-extrusion as shown in Figure 10 and Table 10-2. All films were stored at room conditions of 23 ℃ and 65% RH after being sealed into an aluminum laminated pouch which was filled with nitrogen gas to prevent/reduce the activation by residual oxygen in the pouch.

5.2.2.2. Food simulants

Even though there are no special cosmetic simulants, retinol is a fat-soluble compound and creams in the product generally contain wax / oil components. The inner layer of the OS tubes, which directly contacts the product, is made of linear low density polyethylene (LLDPE) in the polyolefin group. Therefore, the appropriate alternative food simulants recommended by FDA were selected to quantify the major migrant components from the oxygen scavenger in the OS film or tube. The recommended simulants are defined in 21 CFR 176, 170 (c) Table 1 (FDA, 2002) and Appendix 1 as follows:

1) Water and 2) 3% Acetic Acid: From "Food-Type as defined in 21 CFR 176.170 (C) Table 1," the recommended simulant is generally 10% ethanol for aqueous & acidic foods (Food types I, II, IVB, VIB, and VIIB) and Low or High Alcoholic Foods (Food Types VIA and VIC). However, when food acidity is expected to lead to significantly higher levels of migration than with 10% ethanol, or if the polymer or adjuvant is acid-sensitive, separate extractions in water and 3 % acetic acid inlieu of 10% ethanol should be conducted. when food acidity is expected to lead to significantly higher levels of

migration than 10% ethanol, or if the polymer or adjuvant is acid-sensitive. 10% Ethanol is used for Aqueous & Acidic Foods (Food Types I, II, IVB, VIB, and VIIB) Water used was HPLC regent grade (J.T. Baker, Phillipsburg, NJ), and the absolute (100%) acetic acid, Glacial (Mallinckrodt Baker Inc., Phillipsburg, NJ) was diluted with water to make the 3 % solution.

3) Food oil for Fatty Foods (Food Types III, IVA, V, VIIA, and IX): Olive oil (100% pure & natural with no preservatives added) was used as a fatty food simulant. The oil, (FILIPPO BERIO®), which was imported from Italy, was purchased at Meijer.

4) 95% Ethanol: An Effective Fatty-Food Simulant for Polyolefins: The absolute (100%) ethanol (ethyl alcohol, HPLC grade, Sigma-Aldrich,Milwaukee, WI) was diluted with water (HPLC regent grade, J.T. Baker, Phillipsburg, NJ) to make the 95% solution.

5.2.2.3. Migration cell and tube experiments

1) Migration cell

Migration experiments were performed in accordance with ASTM D 4754-98, "Standard Test Method for Two-sided Liquid Extraction of Plastic Materials Using FDA Migration Cell" (ASTM, 1998). The migration cell was prepared as follows: 14 plastic test specimens in the form of round disks, 17.5 mm diameter for each disk, were punched out from the film samples. The total surface area of 14 specimens was calculated as 68.39 cm^2. Then the test specimens were threaded onto a stainless steel wire with alternating glass beads to prevent the specimens from overlapping each other. The threaded specimens on the wire were placed in a 40 ml amber glass vial with a screw top. The food simulant was added into the vial to soak the specimen, a volume of 30 ml. Four vials were prepared for each liquid extractant. Assembled migration cells were stored in a

controlled atmosphere chamber maintained at 40 ℃ for 10 days, following FDA's recommended migration protocols when foods are used at temperatures above the glass transition of polyolefins or room temperature filled and stored without any thermal treatment in the container (FDA/CFSAN, 2007).

2) Migration tube

Migration experiments using tubes were also performed, because of concern that the oxygen scavenger would mainly migrate from the exposed seam in the tube. 3% acetic acid was used as a food simulant, and added into the tube, a volume of 30 ml. Four sets of tubes were heat sealed and coated over-seal with silicone. Total surface area of the inside of tubes in contact with 3% acetic acid was measured and calculated as 52.13 cm^2. Assembled migration tubes were stood up in a holder case and stored in a controlled atmosphere chamber maintained at 40 ℃ for 10 days.

5.2.2.4. Atomic absorption (AA) spectrometry

Quantitative analysis for migrated major components of oxygen scavengers, such as Na, Ca and Fe, in migration cell with food simulants after being stored at 40 ℃ during 10 days was performed using an AA spectrometer (Model Spectr AA-200, Varian, Australia) [Figure 35].

1) Selection of migrant main components

The results of the SEM EDS from Figure 28 and Figure 30 showed that the main components of the residue were NaCl and iron compounds and the main migrants were identified therefore as Na, Cl and Fe. From Figure 32-2, Ca was a minority component but added because it could act to produce the migration of chloride (Cl) as $CaCl_2$.

2) Preparation of standard stock solutions

As standard materials, sodium chloride (NaCl; 99.99%, J.T. Baker, Phillipsburg, NJ), calcium carbonate ($CaCO_3$; AA grade, PerkinElmer) and iron (Fe; AA grade, PerkinElmer) were prepared. 2.542 g of dried NaCl was dissolved in distilled water (HPLC grade, J.T. Baker, Phillipsburg, NJ) and then diluted to 1 liter to give 1,000 μg/ml Na. 2.497 g of dried calcium carbonate in a minimum volume of 1:4 nitric acid was dissolved, and diluted to 1 liter to give 1,000 μg/ml Ca. The solution of iron was prepared by dissolving 1,000 g of iron powder in 20 ml of 1:1 hydrochloric acid and diluting to 1 liter to give 1,000 μg/ml Fe.

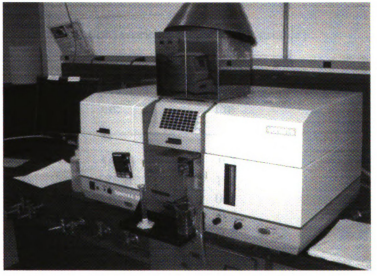


Figure 35. Atomic absorption (AA) spectrometry

3) Instrument parameters

The instrument parameters for the Varian Spectr AA-200 Flame AA Spectrometer, atomic absorptions for fixed and variable working conditions and flame emissions for analysis of Na, Ca and Fe are shown in Table 17, Table 18 and Table 19. The pressures in the gas cylinders were 11 psi for acetylene and 50 psi for air. Fuel flows were all 1.5 L/min. The sample aspiration rate was 5 ml/min, and it took 13 seconds to aspirate 1 ml

of distilled water.

Table 17. Atomic absorption: working conditions (Fixed)

Parameters	Na	Ca	Fe
Lamp current	5 mA	10 mA	5 mA
Fuel	acetylene	acetylene	acetylene
Support	air	nitrous oxide	air
Flame stoichiometry	oxidizing	reducing; red cone 1 – 1.5 cm high	oxidizing

Table 18. Atomic absorption: working conditions (variable)

Major components	Wavelength nm	Slit width nm	Optimum working range μg/ml
Sodium (Na)	589.0	0.5	0.002 – 1.0
	589.6	1.0	0.01 – 2.0
	330.2	0.5	2 – 400
Calcium (Ca)	422.7	0.5	0.01 - 3
Iron (Fe)	248.3	0.2	0.06 - 15

Table 19. Flame emission

Parameters	Na	Ca	Fe
Wavelength	589.0 nm	422.7 nm	372.0 nm
Slit width	0.1 nm	0.1 nm	0.1 nm
Fuel	acetylene	acetylene	acetylene
Support	air	nitrous oxide	air

5.2.2.5. Standard calibration curve

1) Sodium (Na) analysis

Working standard solutions for sodium analysis were prepared by dissolving each volume from the standard stock solution as follows: 0, 1, 3, 5, 8 and 10 ppm (μg/ml) for 95% ethanol; 0, 1, 3, 5, 10, 15 and 20 ppm for distilled water and 3 % acetic acid; 0, 1, 3, 5 ppm for olive oil. After testing the working standard solutions by the AA spectrometer, the standard calibration curve was constructed by calculating the average absorbance of the peaks analyzed three times for each working standard solution. Figure 36 shows the curve for 95% ethanol, Figure 37 shows results for distilled water and 3% acetic acid, and Figure 38 shows olive oil. The best fit equations and corresponding R^2 values for the standard calibration curves for sodium analysis are also shown in Figure 36, 37 and 38. While the R^2 values for 95% ethanol, distilled water and 3% acetic acid were over 0.99, the value for olive oil was a little lower than 0.97.

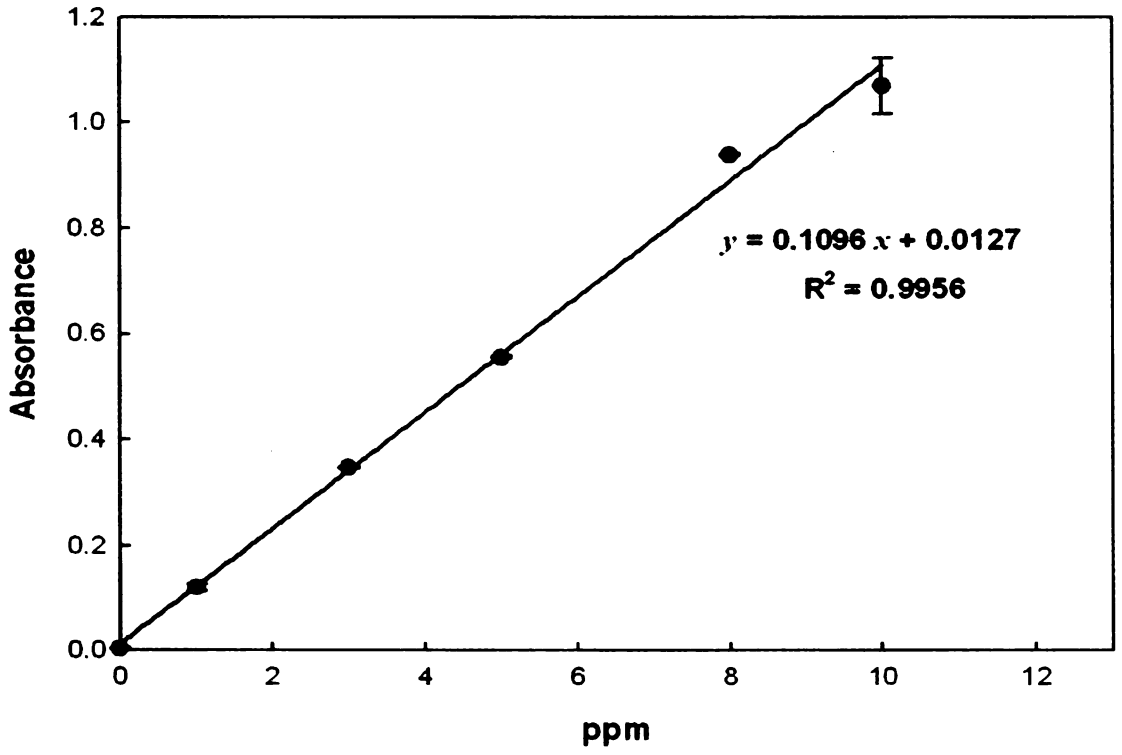


Figure 36. Standard calibration curve for Na concentration in 95% ethanol

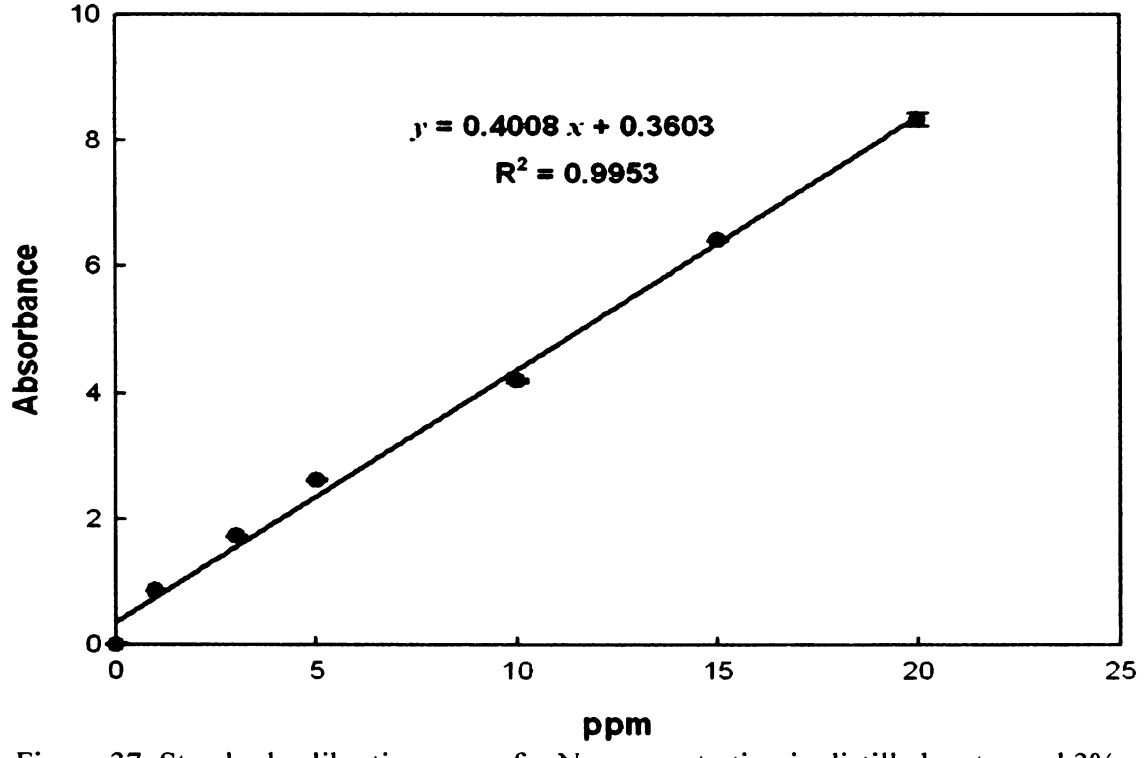


Figure 37. Standard calibration curve for Na concentration in distilled water and 3% acetic acid

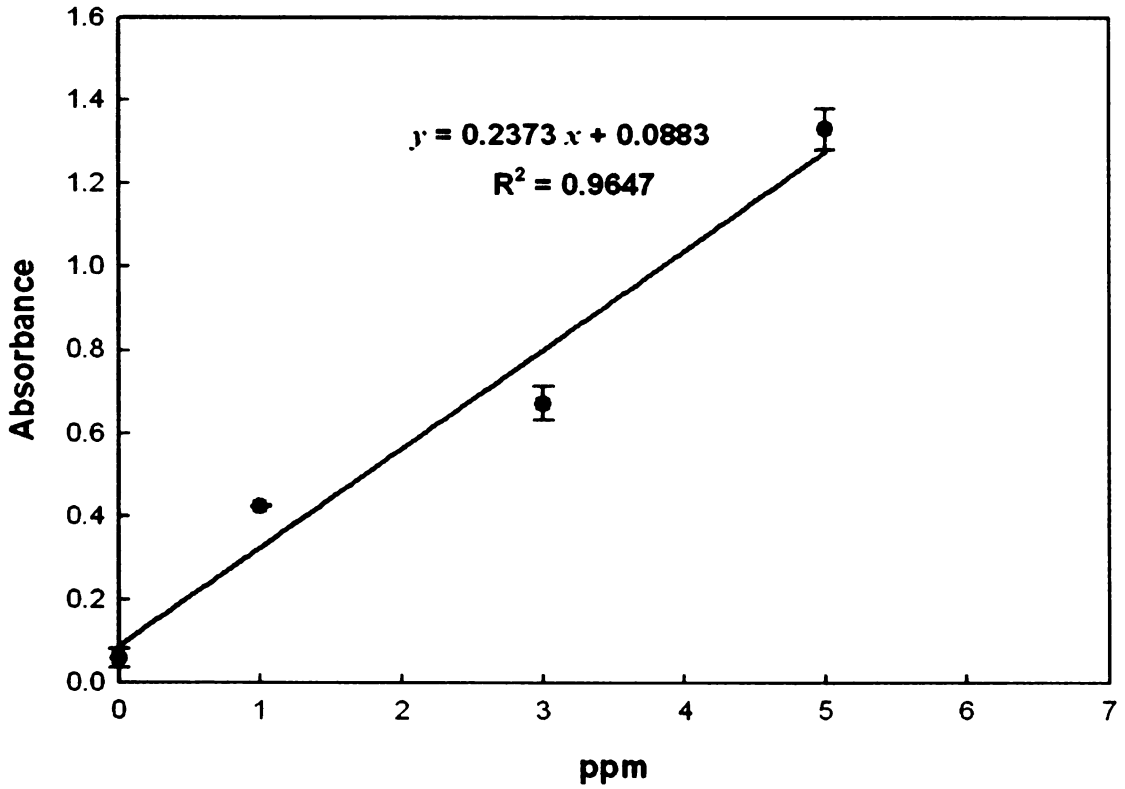


Figure 38. Standard calibration curve for Na concentration in olive oil

2) Calcium (Ca) analysis

Working standard solutions for calcium analysis were prepared by dissolving each volume from the standard stock solution as follows: 0, 1, 3, 5, 8, and 10 ppm (μg/ml) for 95% ethanol, distilled water and 3% acetic acid, and 0, 1, 3, 5 and 10 ppm for olive oil. Figure 39 shows results for 95% ethanol, Figure 40 for distilled water and 3% acetic acid and Figure 41 for olive oil. The best fit equations and corresponding R^2 values for the standard calibration curves for calcium analysis are also shown in Figures 39, 40 and 41.

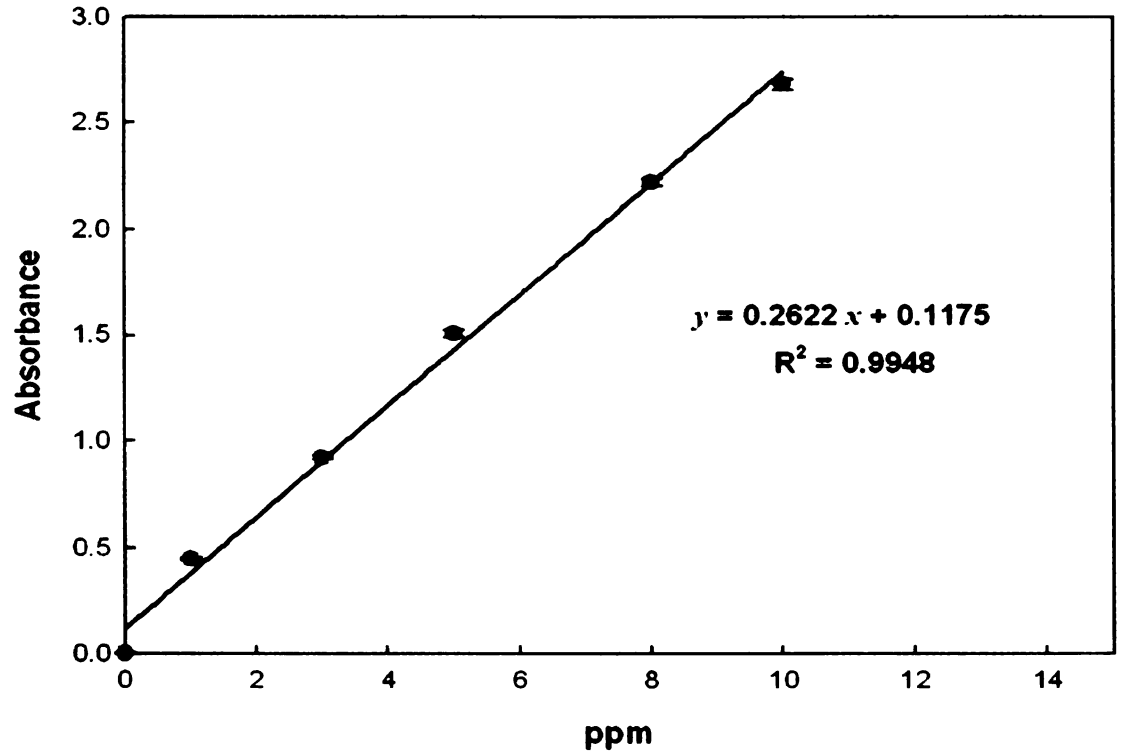


Figure 39. Standard calibration curve for Ca concentration in 95% ethanol

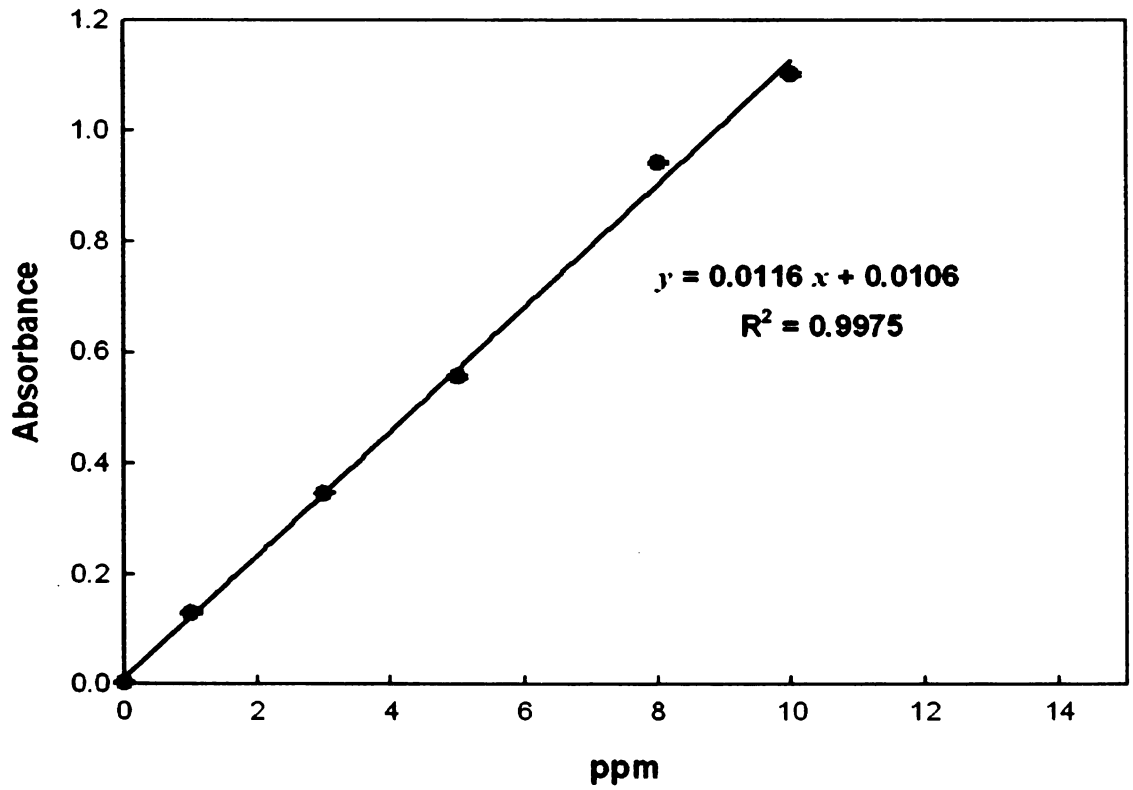


Figure 40. Standard calibration curve for Ca concentration in distilled water and 3% acetic acid

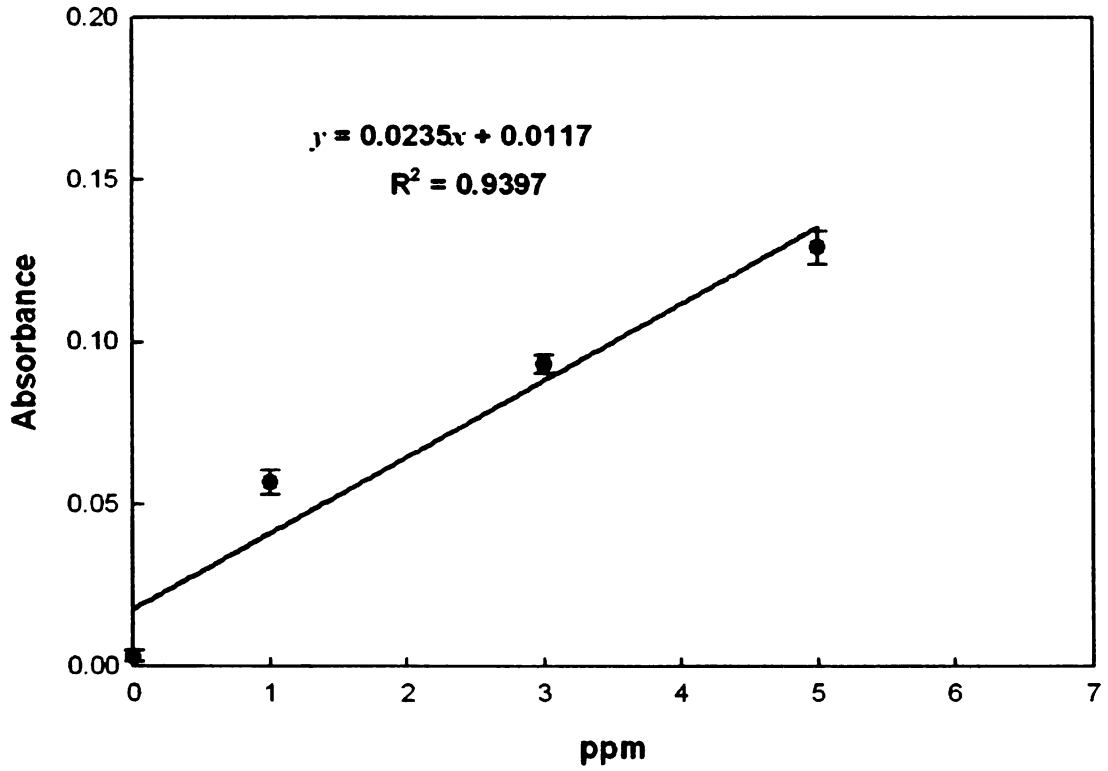


Figure 41. Standard calibration curve for Ca concentration in olive oil

3) Iron (Fe) analysis

Working standard solutions for iron analysis were prepared by dissolving each volume from the standard stock solution as follows: 0, 1, 2, 3, 5, 10 and 20 ppm (μg/ml) for 95% ethanol, distilled water and 3% acetic acid; and 0, 1, 5 and 10 ppm for olive oil. Figure 42 shows results for 95% ethanol, Figure 43 for distilled water and 3% acetic acid and Figure 44 for olive oil. The best fit equations and corresponding R^2 values for the standard calibration curves for iron analysis are also shown in Figures 42, 43 and 44.

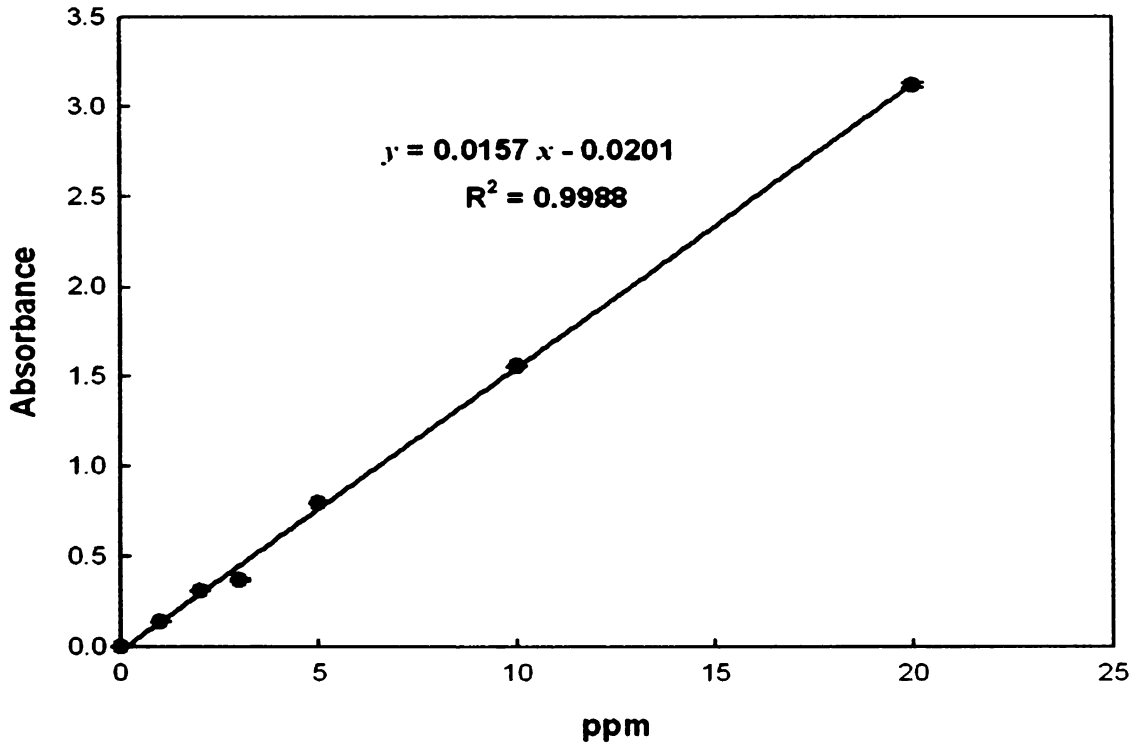


Figure 42. Standard calibration curve for Fe concentration in 95% ethanol

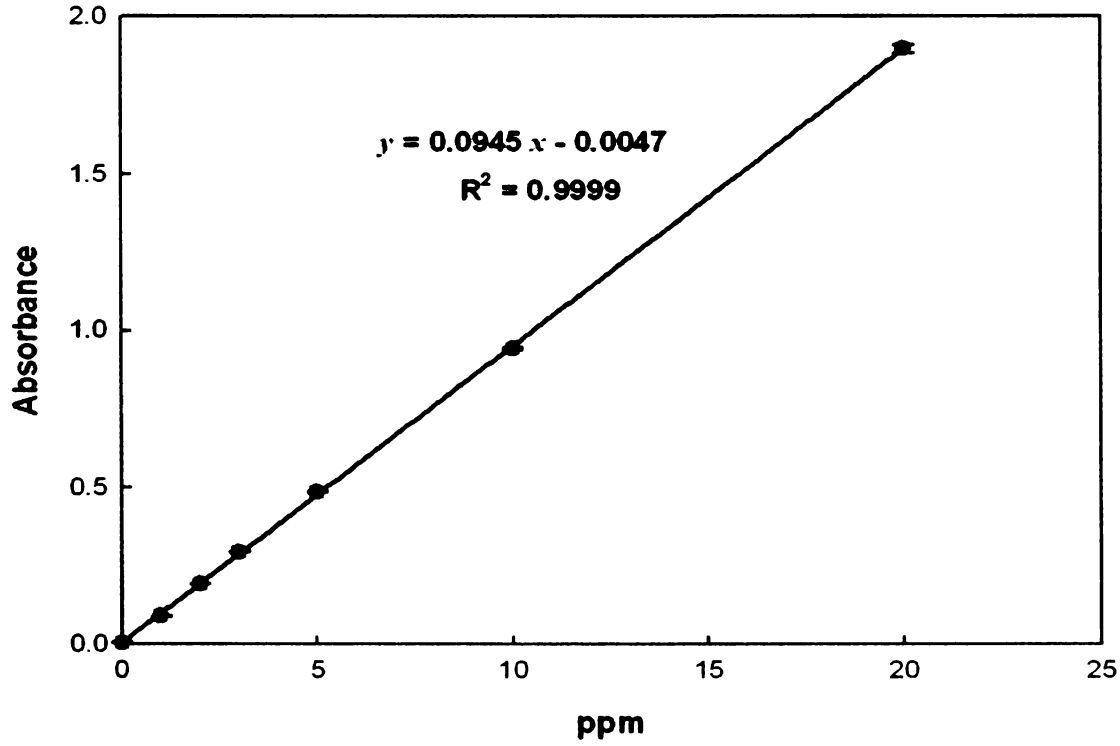


Figure 43. Standard calibration curve for Fe concentration in distilled water and 3% acetic acid

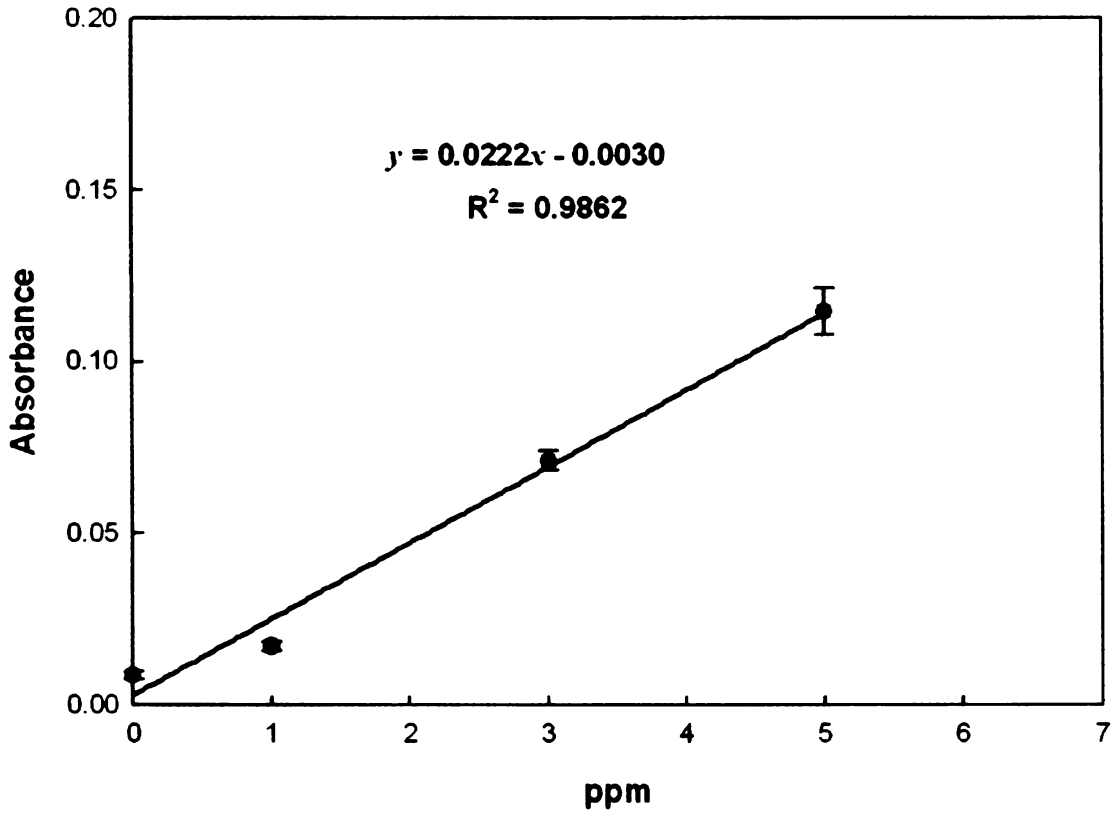


Figure 44. Standard calibration curve for Fe concentration in olive oil

5.3. Results and discussions

In order to observe the migration behavior and evaluate the quantitative analysis of migration for the multilayer oxygen scavenging films, as a first step, the main elements of oxygen scavengers in OS1 and OS2 films were identified. The next step was observation of migration behaviors in the inner layer, which was in direct contact with food simulants or cosmetic, adjacent to the core layer in the specimens and the exposed seam in the tube [Figure 45] using SEM. Finally, the quantitative analysis of migration for the main components of oxygen scavenger in the migration cells was executed using AA spectrometer and compared with tube and sachet type.

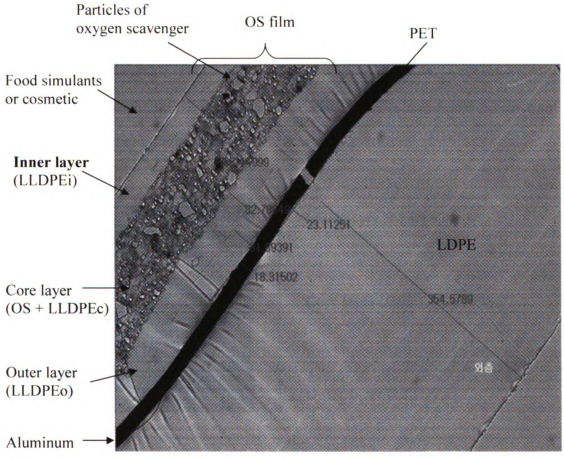


Figure 45. Structure of a tube laminated with the OS film

5.3.1. Observation of migration behaviors

5.3.1.1. Overall migration behaviors in OS films

Figure 46 shows the overall migration behavior for each element of oxygen scavenger in OS1 film that consisted of three layer (LLDPEi/OS1+LLDPEc/LLDPEo), which was snapshotted by the 'X-ray Map' method of SEM EDS and magnified 650 times. The observed elements in OS1 film were iron, silica, chlorine, phosphorus and sodium except carbon and oxygen. The particles of Fe, P, Na and Cl were clearly observed in the core layer (OS1 + LLDPEc) of OS1 film, but they were not seen at all in the inner layer (LLDPEi) or outer layer (LLDPEo). Si was observed both in the core and outer layer. Figure 47 also shows the overall migration behavior for elements (Fe, Si, Cl and Na) of oxygen scavenger in OS2 film, which was snapshotted by same method. The particles of Fe, Si and Cl were observed clearly in the core layer of OS2 film, but they were not seen in the inner or outer layer. In the case of Na, it was not seen even in the core layer. As a result, the main elements (Fe, Na and Cl) of oxygen scavenger were not observed in the inner layer of OS1 and OS2 films by SEM-EDS.

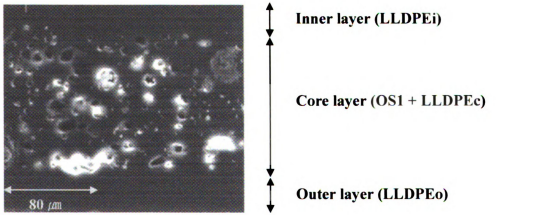
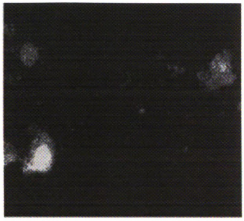
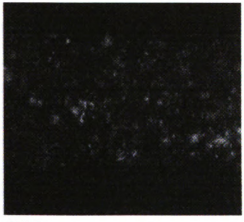


Figure 46. Overall migration behavior for each element of oxygen scavenger in OS1 film by the 'X-ray Map' method of SEM & EDS (Magnified 650 times).

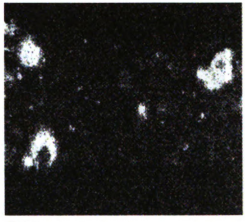


Fe Ka1

Si Ka1



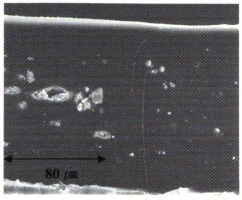
Cl Ka1



P Ka1

Na Ka1_2

Figure 46. *(continued)*

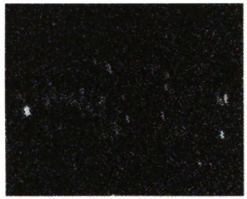


Inner layer (LLDPEi)

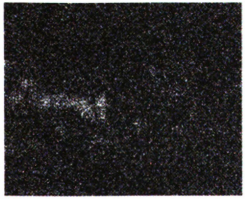
Core layer (OS2 + LLDPEc)

Outer layer (LLDPEo)

Fe Ka1



Si Ka1



Cl Ka1

Na Ka1_2

Figure 47. Overall migration behavior for each element of oxygen scavenger in OS2 film by the 'X-ray Map' method of SEM & EDS (Magnified 650 times).

5.3.1.2. Migration behaviors in the inner layer of OS films

1) Migration behavior into the inner layer of OS1 films

To identify more clearly the migrant behaviors into inner layer for the main elements of oxygen scavenger in the core layer of OS1 films, quantitative analysis at the site of 'Spectrum 1' [Figure 48] in the inner layer, which was in direct contact with food simulants or cosmetic, was executed by the 'Oxford INCA' system of SEM EDS. Figure 49, 50 and 51 shows the result of 'Spectrum 1' in three kinds of OS1 films. As a result, any main elements such as Fe, Na and Cl except C and O from the 'Spectrum 1' in the inner layer of these films were not detected. Furthermore, they were not observed even in 3% acetic acid [Figure 50], which shows the most powerful migration result among food simulants as it mentioned in 5.2.1.1. It means that the main elements of oxygen scavenger in the core layer of OS1 film did not pass through the inner layer and did not contact the food simulants and cosmetic.

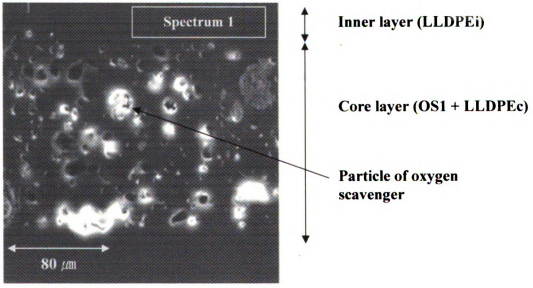
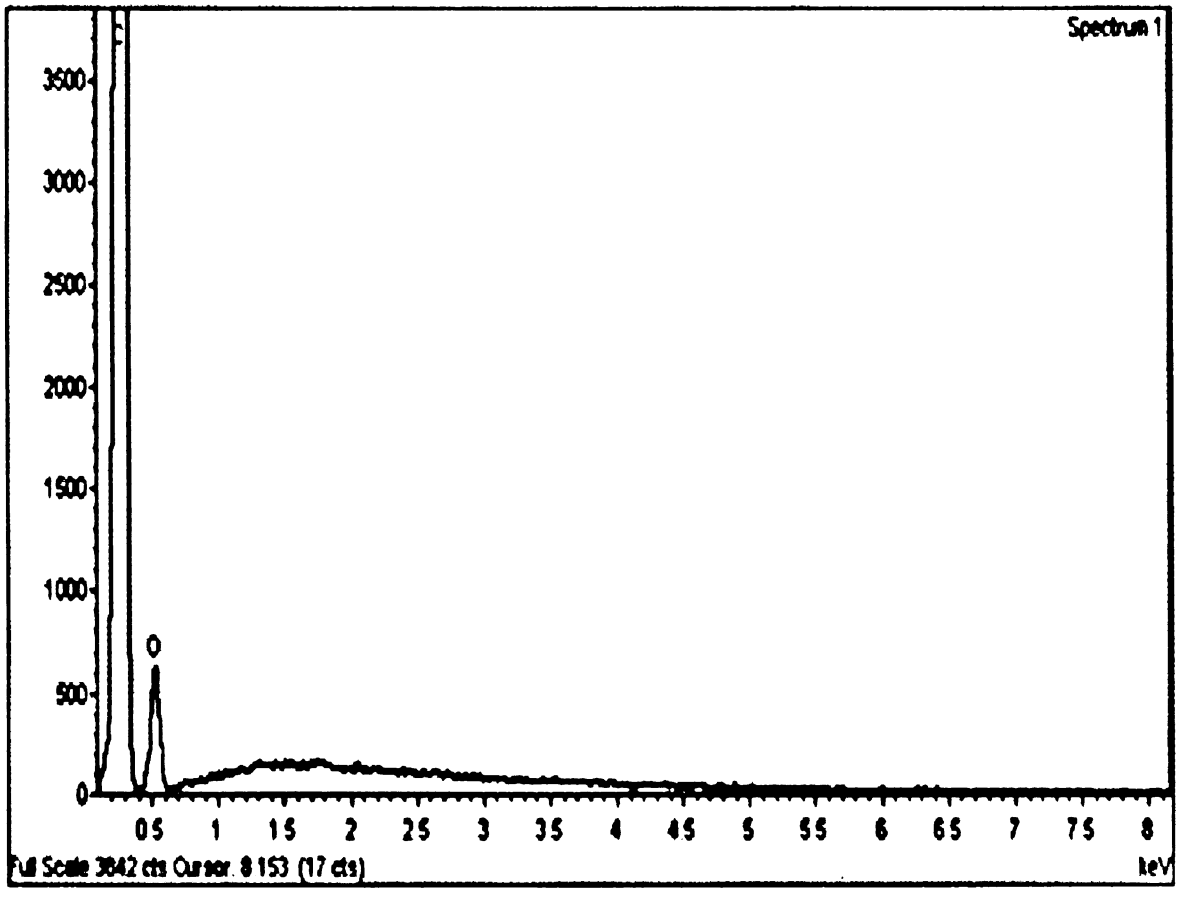
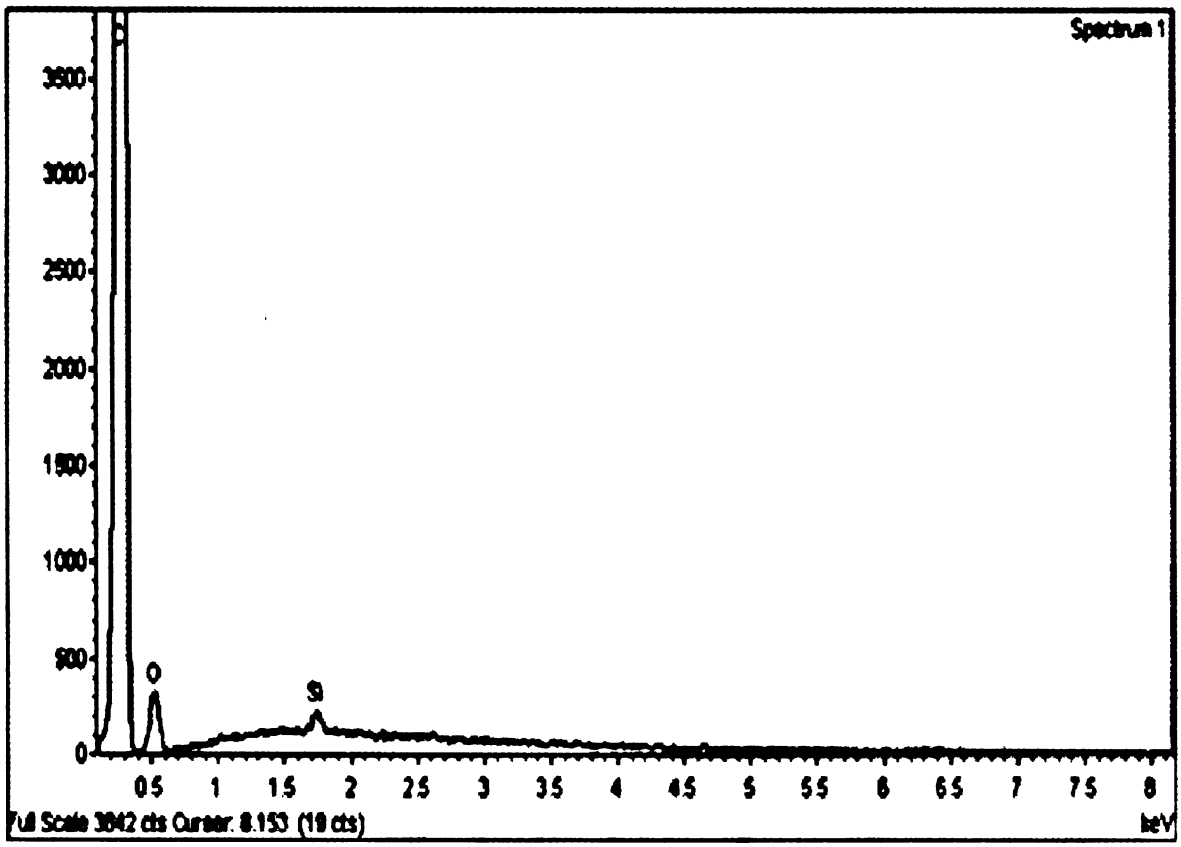


Figure 48. Observation of Spectrum 1 sites of the inner layer of OS1 film



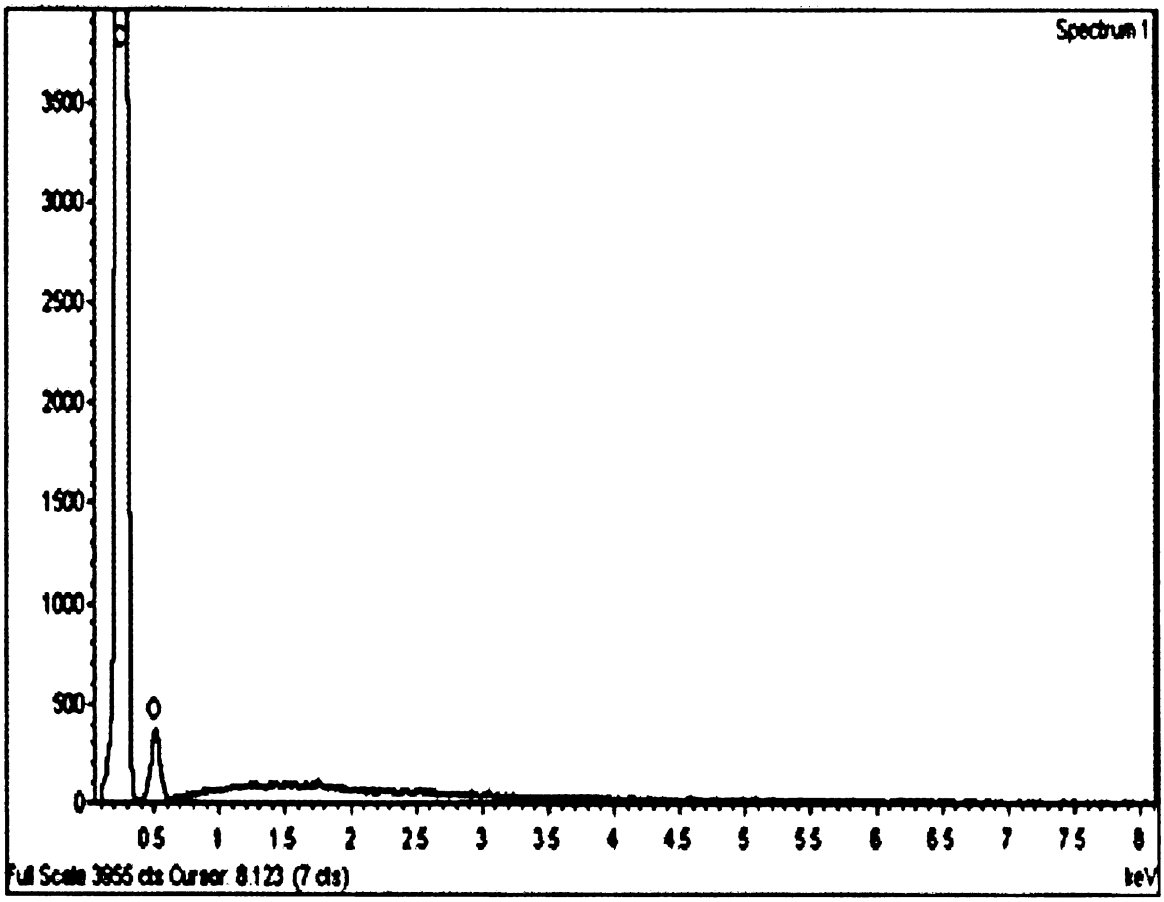
Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	64.72	1.8519	89.32	0.32	91.76
O K	11.66	0.2790	10.68	0.32	8.24
Total			100.00		

Figure 49. Result of Spectrum 1 (OS1 film; 6 months passed at 23 ℃ and 65% RH)



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	46.20	1.8571	91.20	0.35	93.31
O K	6.37	0.2719	8.59	0.35	6.60
Si K	0.57	0.9752	0.21	0.03	0.09
Total			100.00		

Figure 50. Result of Spectrum 1 (OS1 film; stored at 10 days & 40 ℃ in 3% acetic acid)



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	45.55	1.9081	91.42	0.35	93.42
O K	0.61	0.2713	8.58	0.35	6.58
Total			100.00		

Figure 51. Result of Spectrum 1 (OS1 film; 6 months passed in room conditions after filling cosmetic)

2) Migration behavior into the inner layer of OS2 film

Observations of migration behaviors into the inner layer of OS2 films were executed by the same method as that for OS1 film in Figure 52. As can be seen in Figures 53, 54 and 55, no migration of the main elements (Fe, Na and Cl) of oxygen scavenger into the inner layer (site of 'Spectrum 1') was observed. This was the same result as that of OS1, and it means that the main elements of oxygen scavenger in the core layer of OS2 film did not pass through the inner layer and did not contact the food simulants and cosmetic. Si was seen in both inner layers, which were made of LLDPE, in OS1 and OS2 film as a minor element, which might be due to silicone oil from screen changers in the blown film process or additives in the polymer.

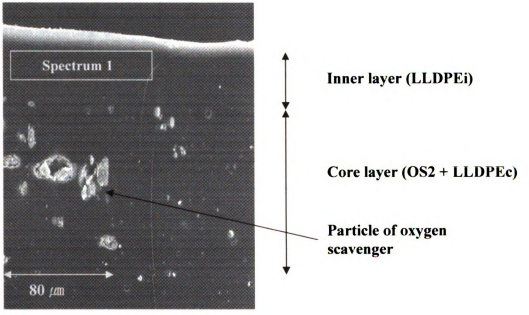
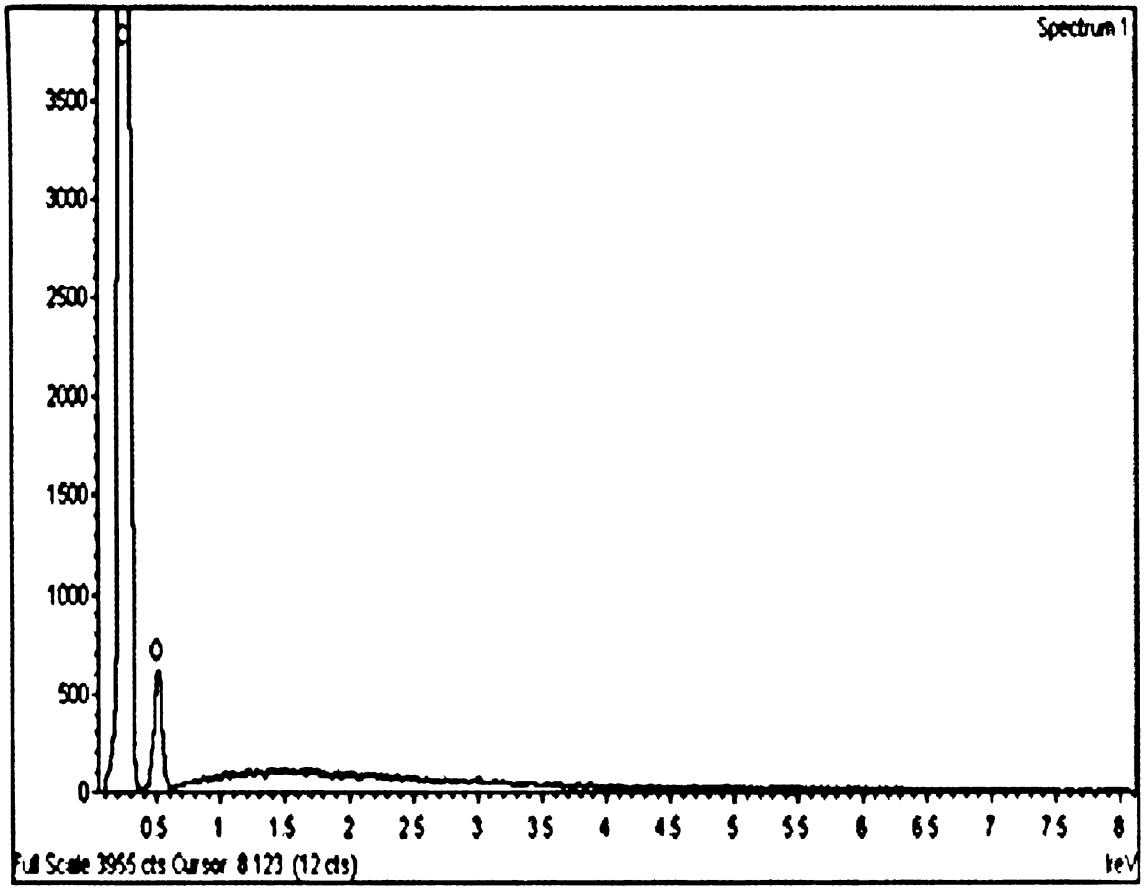
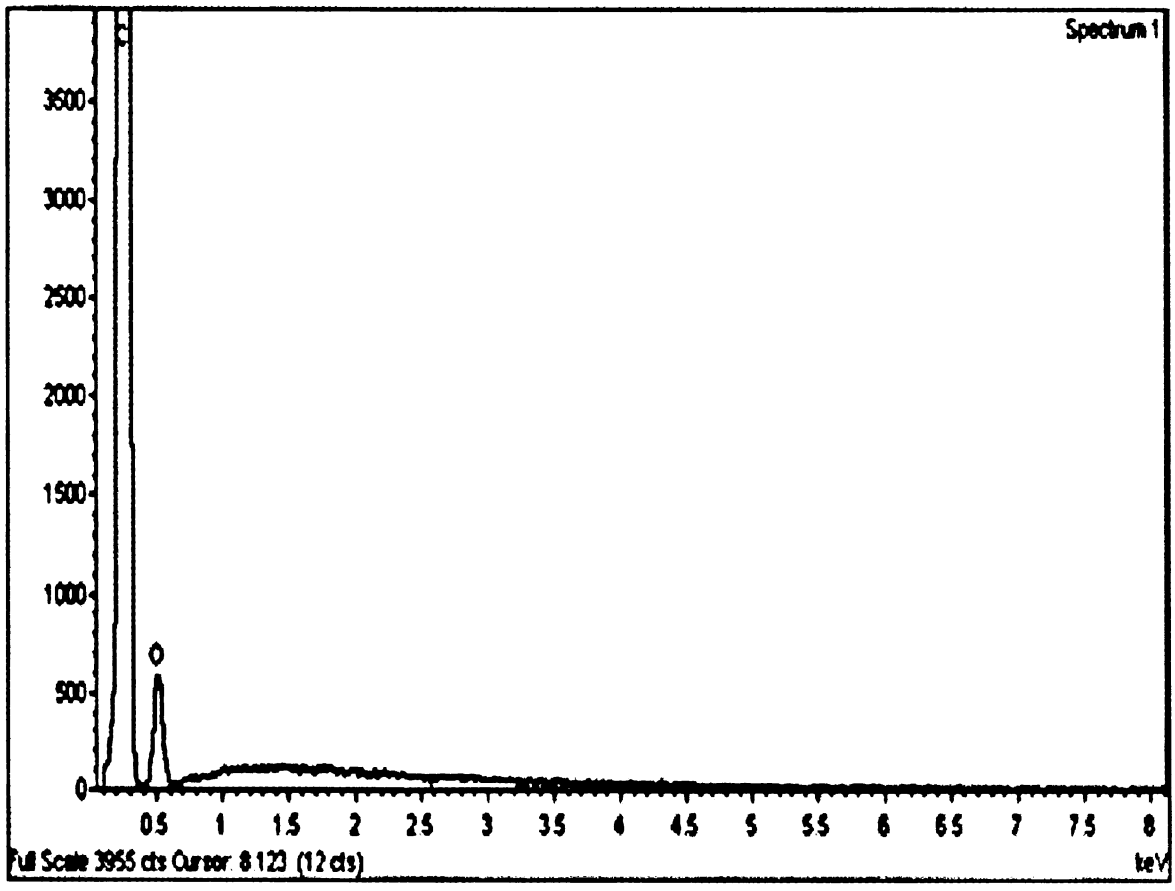


Figure 52. Observation of Spectrum 1 sites of in the inner layer of OS2 film



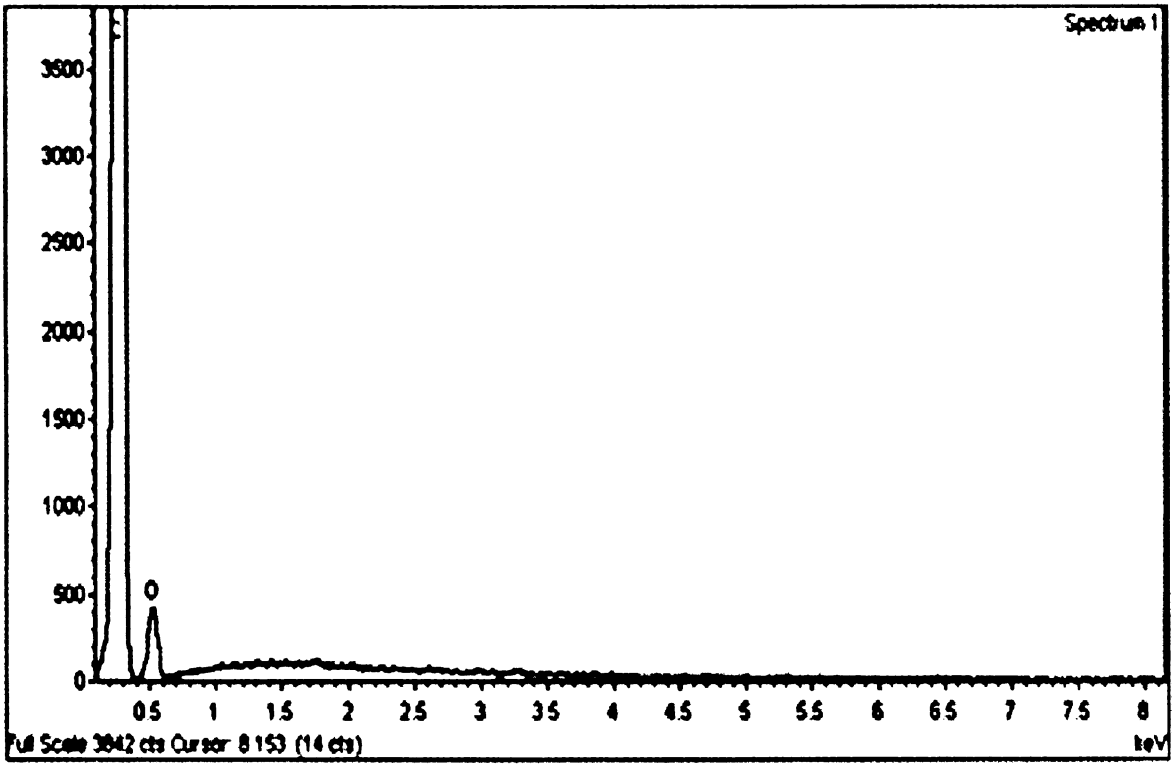
Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	43.54	1.7854	86.65	0.35	89.63
O K	1.09	0.2892	13.35	0.35	10.37
Total			100.00		

Figure 53. Result of Spectrum 1 (OS2 film; 6 months passed at 23 ℃ and 65% RH)



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	54.18	1.8476	89.15	0.33	91.63
O K	1.00	0.2796	10.85	0.33	8.37
Total			100.00		

Figure 54. Result of Spectrum 1 (OS2 film; stored at 10 days & 40 ℃ in 3% acetic acid)



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	55.46	1.8909	90.81	0.34	92.94
O K	8.12	0.2736	9.19	0.34	7.06
Total			100.00		

Figure 55. Result of Spectrum 1 (OS2 film; 6 months passed in room conditions after filling cosmetic)

5.3.1.3. Migration behaviors in a tube

As is shown in Figure 45 in Section 5.3, the inside of a tube containing food simulants or cosmetic mostly consisted of the inner layer (LLDPEi) of OS films, but the seamed parting line of the tubes also contacted the simulants. This means that the oxygen scavengers in the seamed parting line had a possibility to be exposed directly to the simulants [Figure 56]. Therefore, the migration behaviors in the inner layer and the seamed parting line in a tube were observed by SEM & EDS. From Figure 57, 'Spectrum 1' was the seamed parting line and 'Spectrum 2' was the inner layer in a tube which was stored at 10 days and 40 ℃ after filling with 3% acetic acid. While the main elements such as Fe, Na and Cl could be observed in 'Spectrum 1' [Figure 58], these elements were not seen in "Spectrum 2' [Figure 59]. Therefore, the main elements of oxygen scavenger migrated through the seamed parting line in a tube exposed directly to the simulants.

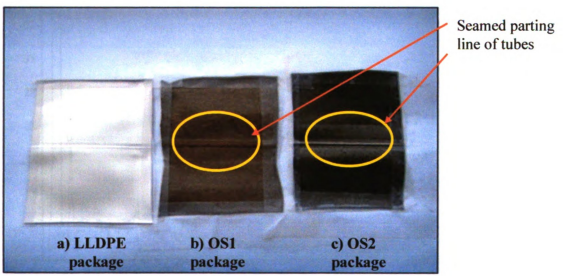


Figure 56. Inside of package after 6 months passed in room conditions after filling cosmetic; the seamed parting line of OS1 and OS2 packages are darker than the other inside area because it is more oxidized by directly contacting the oxygen in the cosmetic or headspace of a package. This means that main components of oxygen scavenger in the seamed parting line are able to migrate more easily to simulants.

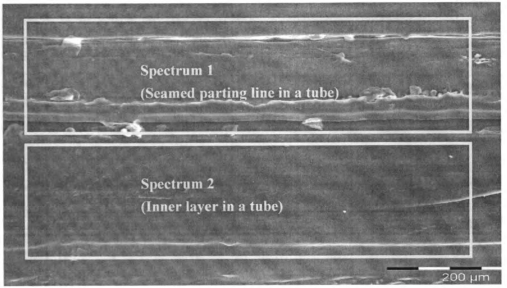


Figure 57. Spectrum sites for inside of a tube by SEM EDS

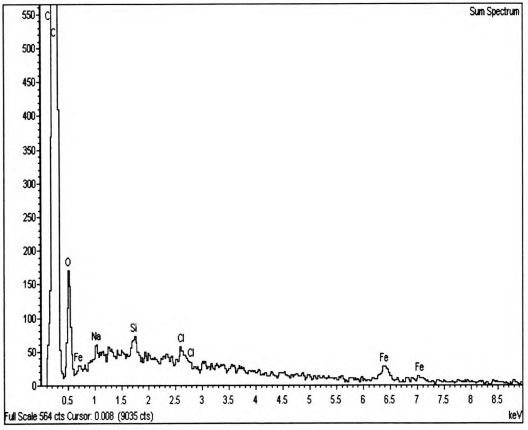
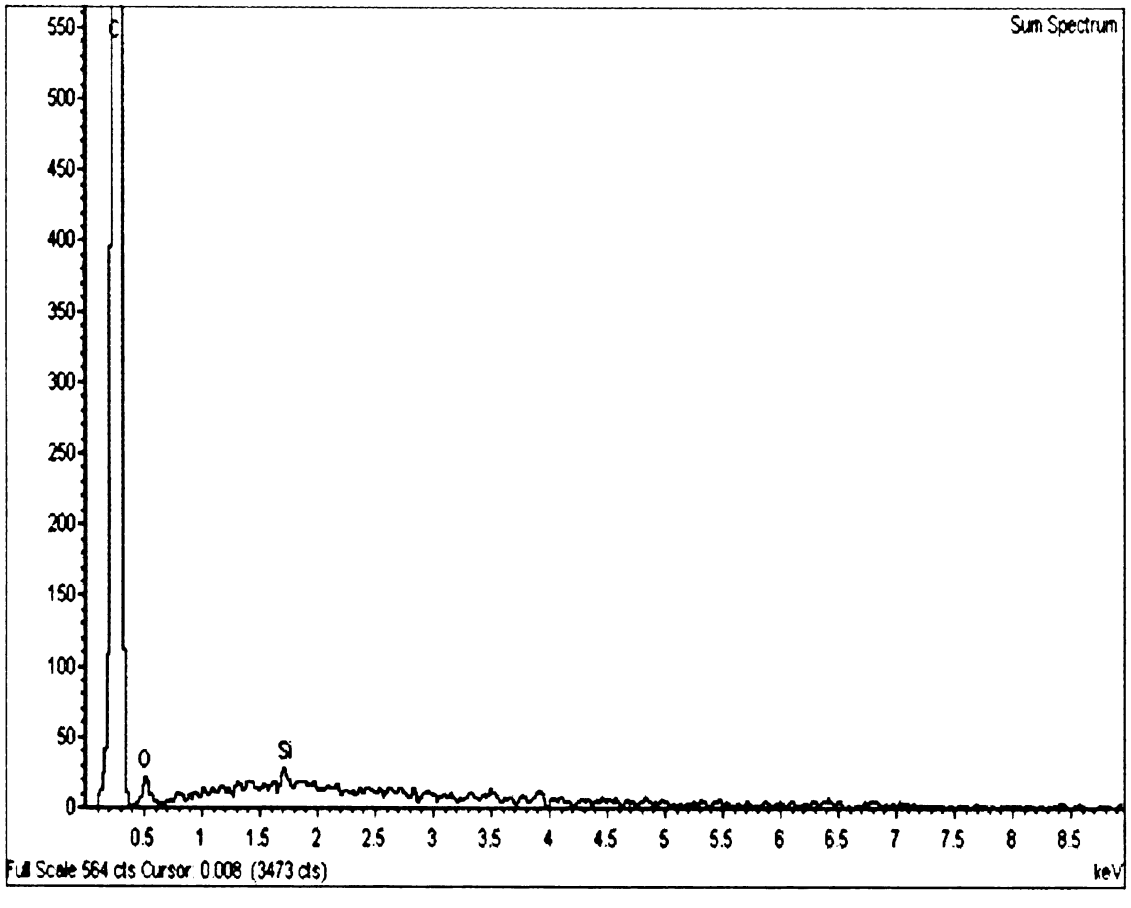


Figure 58. Result of Spectrum 1 (Seamed parting line in a tube; stored at 10 days and 40 ℃ in 3% acetic acid)

Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	55.80	1.8313	91.32	0.59	93.60
O K	7.31	0.2716	8.06	0.58	6.20
Na K	0.22	0.9068	0.07	0.06	0.04
Si K	0.35	0.9731	0.11	0.04	0.05
Cl K	0.22	0.8422	0.08	0.04	0.03
Fe K	0.91	0.7712	0.36	0.08	0.08
Total			100.00		

Figure 58. *(continued)*



Element	App Conc.	Intensity Comp.	Weight %	Weight % Sigma	Atomic %
C K	49.34	2.0007	95.80	1.10	96.86
O K	2.68	0.2566	4.06	1.10	3.08
Si K	0.34	0.9879	0.13	0.10	0.06
Total			100.00		

Figure 59. Result of Spectrum 2 (Inner layer in a tube; stored at 10 days and 40 ℃ in 3% acetic acid)

5.3.2. Quantitative analysis of migration by AA spectrometry

Throughout the observation of migration behaviors in the OS films and tube by SEM & EDS, the main elements of oxygen scavenger were migrated from the seamed parting line to expose directly to the simulants. This appearance seems to be able to occur in the migration vials because the edge of core layer of the film sample, which contains oxygen scavenger, also directly exposed to the simulants. Therefore, quantitative analysis of migration to the migration vials and tubes in various food simulants was executed using AA spectrometry.

5.3.2.1 Migration result for Na and calculation for NaCl

Table 20 shows the values (μg) of sodium which migrated into various food simulants in the migration vials, and Table 21 shows the migration value of NaCl as calculated from observed migration of sodium. OS1 has much higher values for water (17.8 μg/30 ml in migration of sodium) and 3% acetic acid (17.4 μg/30 ml in migration of sodium), which are more than 6 times than those of LLDPE. The values of OS2 are overall less than 5 μg/30 ml in migration of sodium or 0.4 mg/L in migration of sodium chloride for all food simulants. LLDPE has some migration values that are not 0. This may be due to additives in the polymer. As a whole, the migration values in 95% ethanol, water and 3% acetic acid are significantly different between OS1, OS2 and LLDPE, but the value in olive oil is not significantly different between them.

Table 20. Migration of sodium (Na) into food simulants

(Unit: μg/30 ml)

Sample		95 % Ethanol	Water	3% Acetic Acid	Olive Oil
OS1	Ave	3.489	17.805	17.408	0.497
	Std	0.170	0.229	0.384	0.249
	Dev	1a	2a	3a	4a
OS2	Ave	1.199	3.608	4.273	0.427
	Std	0.100	0.254	0.238	0.064
	Dev	1b	2b	3b	4a
LLDPE	Ave	0.521	2.145	2.831	0.513
	Std	0.074	0.186	0.246	0.210
	Dev	1c	2c	3c	4a

n = 12; 4 specimens x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).

Table 21. Specific migration of NaCl as calculated from observed migration of sodium, respectively.

(Unit: mg/L)

Sample		95 % Ethanol	Water	3% Acetic Acid	Olive Oil
OS1	Ave	0.297	1.508	1.476	0.043
	Std	0.014	0.019	0.032	0.021
	Dev	1a	2a	3a	4a
OS2	Ave	0.100	0.305	0.363	0.034
	Std	0.007	0.022	0.019	0.007
	Dev	1b	2b	3b	4a
LLDPE	Ave	0.045	0.181	0.239	0.043
	Std	0.005	0.017	0.021	0.018
	Dev	1c	2c	3c	4a

n = 12; 4 specimens x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).

Specific migration of NaCl is calculated from observed migration of sodium as follows;

$$ppmNaCl = \frac{ppmNa^{+} \times 58.44 \frac{g}{moleNaCl}}{23 \frac{g}{moleNa^{+}}} \quad (5.1)$$

5.3.2.2. Migration result for Ca and calculation for $CaCl_2$

Table 22 shows the values (μg) of calcium which migrated into various food simulants in the migration vials, and Table 23 shows the migration value of $CaCl_2$ as calculated from observed migration of calcium. OS1 and LLDPE have very low level that are less than 0.5 μg/30 ml or 0.05 mg/L in migration of calcium or calcium chloride for all food simulants, but OS2 shows much higher values in migration than other two for water, 3 % acetic acid and olive oil. The highest value of OS2 is 4.507 μg/30 ml in migration of calcium or 0.418 mg/L in migration of calcium chloride for 3% acetic acid.

Table 22. Migration of calcium (Ca) into food simulants

(Unit: μg/30 ml)

Sample		95 % Ethanol	Water	3% Acetic Acid	Olive Oil
OS1	Ave	- 0.382	0.049	0.302	0.492
	Std	0.011	0.018	0.038	0.471
	Dev	1a	2a	3a	4a
OS2	Ave	- 0.371	0.630	4.507	1.320
	Std	0.010	0.326	0.371	0.569
	Dev	1a	2b	3b	4b
LLDPE	Ave	- 0.342	0.297	0.326	0.484
	Std	0.010	0.116	0.119	0.250
	Dev	1a	2ab	3a	4a

n = 12; 4 specimens x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).
Negative values less than 1 ppm can be considered 0 as a test error.

Table 23. Specific migration of $CaCl_2$ as calculated from observed migration of calcium, respectively.

(Unit: mg/L)

Sample		95 % Ethanol	Water	3% Acetic Acid	Olive Oil
OS1	Ave	- 0.037	0.001	0.028	0.045
	Std	0.005	0.003	0.004	0.045
	Dev	1a	2a	3a	4a
OS2	Ave	- 0.033	0.020	0.418	0.123
	Std	0.005	0.034	0.034	0.054
	Dev	1a	2b	3b	4b
LLDPE	Ave	- 0.030	0.009	0.029	0.047
	Std	0.000	0.014	0.013	0.024
	Dev	1a	2ab	3a	4a

n = 12; 4 specimens x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).
Specific migration of $CaCl_2$ is calculated from observed migration of calcium as follows;

$$ppmCaCl_2 = \frac{ppmCa^{++} \times 111.0 \; \frac{g}{moleCaCl_2}}{40 \; \frac{g}{moleCa^{++}}} \qquad (5.2)$$

5.3.2.3. Migration result for Fe and calculation for Fe_2O_3

Table 24 shows the values (μg) of iron which migrated into various food simulants in the migration vials, and Table 25 shows the migration value of Fe_2O_3 as

calculated from observed migration of iron. OS1 is the highest value (17.176 μg/30 ml) for 3 % acetic acid, which are almost two orders of magnitude greater than that of LLDPE (0.295 μg/30 ml). The values of OS2 is 3.072 μg/30 ml in migration of iron and calculated 0.818 mg/L in migration of iron oxide for 3% acetic acid. LLDPE has some migration value but less than 0.3 μg/30 ml, it may be due to impurities from the extrusion process or punching to make disks in migration vials. As a whole, the migration values in 3% acetic acid are significantly different between OS1, OS2 and LLDPE, but the values in 95% ethanol and olive oil are not different between them.

Table 24. Migration of iron (Fe) into food simulants

(Unit: μg/30 ml)

Sample		95 % Ethanol	Water	3% Acetic Acid	Olive Oil
OS1	Ave	0.136	1.811	17.176	0.299
	Std	0.008	0.257	1.735	0.333
	Dev	1a	2a	3a	4a
OS2	Ave	0.138	- 0.004	3.072	0.185
	Std	0.009	0.021	0.168	0.161
	Dev	1a	2b	3b	4a
LLDPE	Ave	0.143	- 0.019	0.295	0.225
	Std	0.008	0.018	0.022	0.056
	Dev	1a	2b	3c	4a

n = 12; 4 specimens x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).
Negative values less than 1 ppm can be considered 0 as a test error.

Table 25. Specific migration of Fe_2O_3 is calculated from observed migration of iron, respectively.

(Unit: mg/L)

Sample		95 % Ethanol	Water	3 % Acetic Acid	Olive Oil
OS1	Ave	0.010	0.028	0.818	0.015
	Std	0.000	0.042	0.083	0.015
	Dev	1a	2a	3a	4a
OS2	Ave	0.010	0.000	0.148	0.009
	Std	0.000	0.000	0.009	0.009
	Dev	1a	2b	3b	4a
LLDPE	Ave	0.010	0.000	0.012	0.011
	Std	0.000	0.000	0.004	0.003
	Dev	1a	2b	3c	4a

n = 12; 4 specimens x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).
Specific migration of Fe_2O_3 is calculated from observed migration of iron as follows;

$$ppmFe_2O_3 = \frac{ppmFe^{+++} \times 159.7 \ \frac{g}{moleFe_2O_3}}{111.7 \ \frac{g}{moleFe^{+++}}} \qquad (5.3)$$

5.3.2.4. Results for the sum of migration for main components in migration vials

The sum of migration in the migration vials for the main elements (Na + Ca + Fe) are compared in Table 26. As a whole, the migration values in 3% acetic acid are the highest and the next are those in water, among the food simulants. The migration values in 95% ethanol, water and 3% acetic acid are significantly different between OS1, OS2 and LLDPE, but the value in olive oil is not significantly different between them. OS1 has the highest value (34.885 μg/30 ml) for 3% acetic acid, which is almost 10 times

greater than that of LLDPE (3.452 μg/30 ml) and near to 3 times that of OS2 (11.852 μg/30 ml). The sum of migration (19.665 μg/30 ml) of OS1 for water also has a very high value.

The sum of migration for NaCl + $CaCl_2$ + Fe_2O_3 from Table 27, OS1 is 2.322 mg/L for 3 % acetic acid, which is the highest value among the food simulants. However, it is less than the EU limit for total migration of 60 mg/L (90/128/EEC).

Table 26. Sum of migration for main elements (Na + Ca + Fe)

(Unit: μg/30 ml)

Sample		95 % Ethanol	Water	3% Acetic Acid	Olive Oil
OS1	Ave	3.243	19.665	34.885	1.288
	Std	0.168	0.435	1.441	0.612
	Dev	1a	2a	3a	4a
OS2	Ave	0.966	4.234	11.852	1.932
	Std	0.097	0.509	0.357	0.631
	Dev	1b	2b	3b	4a
LLDPE	Ave	0.322	2.423	3.452	1.223
	Std	0.073	0.159	0.316	0.328
	Dev	1c	2c	3c	4a

n = 36; 4 specimen x 3 replicates x 3 elements
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).

Table 27. Sum of migration for main components (NaCl + $CaCl_2$ + Fe_2O_3) as calculated from observed migration of sodium, calcium and iron, respectively.

(Unit: mg/L)

Sample		95 % Ethanol	Water	3% Acetic Acid	Olive Oil
OS1	Ave	0.270	1.538	2.322	0.102
	Std	0.017	0.047	0.062	0.046
	Dev	1a	2a	3a	4a
OS2	Ave	0.078	0.325	0.928	0.167
	Std	0.009	0.043	0.036	0.056
	Dev	1b	2b	3b	4a
LLDPE	Ave	0.025	0.190	0.280	0.100
	Std	0.005	0.022	0.028	0.030
	Dev	1c	2c	3c	4a

n = 36; 4 specimen x 3 replicates x 3 components

Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).

Specific migration of NaCl, $CaCl_2$ and Fe_2O_3 is calculated from the observed migration of sodium, calcium and iron as follows;

$$ppmNaCl = \frac{ppmNa^{+} \times 58.44 \ \frac{g}{moleNaCl}}{23 \ \frac{g}{moleNa^{+}}},$$

$$ppmCaCl_2 = \frac{ppmCa^{++} \times 111.0 \ \frac{g}{moleCaCl_2}}{40 \ \frac{g}{moleCa^{++}}}$$

$$ppmFe_2O_3 = \frac{ppmFe^{+++} \times 159.7 \ \frac{g}{moleFe_2O_3}}{111.7 \ \frac{g}{moleFe^{+++}}}$$

5.3.2.5. Color change of the films after migration test in various food simulants

Figure 60 shows the changed color of the films used for migration tests in various food simulants. While OS1 in 3% acetic acid was the most changed, to dark red from a gray color, and the sample of OS2 in 3 % acetic acid looked like mixed a dark red color in its original black color to compare with other samples, samples of LLDPE were transparent and not changed in color. The reason that the migration value was high in 3% acetic acid and in distilled water is that they are hydrophilic (polar) protic solvents. Especially, acetic acid (CH_3COOH) is a week, effectively monoprotic acid in aqueous solution. The hydrogen (H) atom in the carboxyl group (-COOH) in carboxylic acids such as acetic acid can be given off as an H^+ ion (proton), giving them their acidic character. Due to this chemical property, acetic acid is corrosive to metals including iron or metal salts in oxygen scavenger and results in a deeply red color as a iron (III) chloride solution (Cambridge Encyclopedia, 2009).

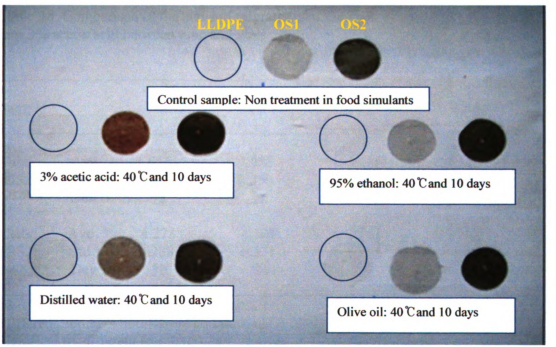


Figure 60. Color change of the films used as migration disks after migration test

5.3.2.6. Comparison of the migration of the main components in tubes and vials

The sums of migrations for tubes and vials that were made of OS2 for the main elements (Na, Ca and Fe) and the main components (NaCl, $CaCl_2$ and Fe_2O_3) are compared in Tables 28 and 29. The values are only evaluated in 3 % acetic acid because of its highest value among other food simulants. The sum is 5.131 μg/30 ml for migrated main elements and 0.398 mg/L for migrated main components in tubes. In cells, the sum is 11.852 μg/30 ml for migrated main elements and 0.928 mg/L for migrated main components. For Table 30, the inside area of the tube in contact with 3% acetic acid was calculated as 52.13 cm^2, and the total surface of migration samples in a vial was calculated as 68.39 cm^2. If the inside area of the tube is recalculated as the same as the total surface of the migration samples, the value of migrated main components from the inside of the tube would be 0.522 mg/L. This means that the value of from the migration samples in the vials (0.928 mg/L) is near to 2 times that of the tubes.

Table 28. Comparison of the sums of migrations of the main elements (Na, Ca and Fe) into 3% acetic acid between tube and vials

(Unit: μg/30 ml)

Sample		Na	Ca	Fe	Sum
Tube	Ave	1.655	2.088	1.389	5.131
(OS2)	Std	0.444	0.350	0.232	0.495
	Dev	1a	2a	3a	4a
Cells	Ave	4.273	4.507	3.072	11.852
(OS2)	Std	0.238	0.371	0.168	0.357
	Dev	1b	2b	3b	4b

n= 12 for cells; 4 specimen x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).

Table 29. Comparison of the sums of migrations for the main components (NaCl, $CaCl_2$ and Fe_2O_3) into 3% acetic acid between tubes and vials as calculated from observed migration of sodium, calcium and iron, respectively.

(Unit: mg/L)

Sample		NaCl	$CaCl_2$	Fe_2O_3	Sum
Tube (OS2)	Ave	0.139	0.194	0.065	0.398
	Std	0.038	0.033	0.009	0.050
	Dev	1a	2a	3a	4a
Cells (OS2)	Ave	0.363	0.418	0.148	0.928
	Std	0.019	0.034	0.009	0.036
	Dev	1b	2b	3b	4b

n= 12 for cells; 4 specimen x 3 replicates
Different numbers in different columns and different letters within a column are significantly different ($p < 0.05$).

Table 30. Comparison of the sums of migrations for the main components (NaCl, $CaCl_2$ and Fe_2O_3) into 3% acetic acid between tubes and vials including calculated values normalized to the same surface area

Sample	Total surface	Sum of migration
Cells	68.39 cm^2 [1)]	0.928 mg/L
Tube	52.13 cm^2 [2)]	0.398 mg/L
Normalized	68.39 cm^2	0.522 mg/L[3)]

1) $2\pi r_1$ x ht = 2 x 3.1416 x 1.22 cm x 6.8 cm = 52.13 cm^2
2) 14 pieces x (πr_2^2x 2 + $2\pi r_2$ x hc) = 14 x (3.1416 x 0.875 cm^2 x 2 + 2 x 3.1416 x 0.875 cm x 0.0135 cm) = 68.39 cm^2
3) 0.398 mg/L x (68.39 cm^2/52.13 cm^2) = 0.522 mg/L

This seems to be due to the fact that the total area of the exposed edge of the migration samples in the vial that contacts the food simulants was larger than that of the seamed parting line in the tube.

5.4. Summary

This investigation of the migration behavior of the oxygen scavenger in active packaging can be summarized as follows:

1) From the observation of overall migration in the OS film for the main elements (Fe, Na and Cl) of the oxygen scavenger by the 'X-ray Map' method of SEM EDS, the main elements were observed clearly in the core layer of OS film, but they were not seen in the inner and outer layers.

2) Throughout the observation of the migration behavior for the main elements by the SEM & EDS, no migration of any of these main elements was detected in the inner layer adjacent to the core layer containing oxygen scavenger of the OS multilayer films (OS1 and OS2), which was direct contact with food simulants or cosmetic. This means that the main elements of oxygen scavenger in the core layer of the OS films did not pass through the inner layer and did not contact the food simulants and cosmetic.

3) From another analysis by SEM & EDS for the seamed parting line in a tube that was stored at 10 days and 40 ℃ in 3% acetic acid, the main elements (Fe, Na and Cl) could be observed. However, the main elements were not detected on the non seamed area in the inside of a tube. Therefore, the main elements of oxygen scavenger migrated from the seamed parting line that was exposed directly to the simulants.

4) From the quantitative analysis of migration of the main components ($NaCl+CaCl_2+Fe_2O_3$) from migration vials into various food simulants by AA spectrometer, the migration values in 3% acetic acid were the highest and the next were the values in water among the food simulants. The migration value of OS1 in 3% acetic acid was as 2.322 mg/L, OS2 was 0.928 mg/L and LLDPE was 0.280 mg/L. However, these values are much less than the EU limit for total migration of 60 mg/L (90/128/EEC).

5) From the quantitative analysis for the sums of migration in 3% acetic acid between tubes and cells which were made of OS2 film, the value of migrated main components ($NaCl+CaCl_2+ Fe_2O_3$) in the tube was 0.398 mg/L, and the value in migration cells was 0.928 mg/L. If the inside area of the tube is recalculated as the same as the total surface of migration cells, the value of migrated main components from the inside of the tube would be 0.522 mg/L. This means that the value in the migration cells (0.928 mg/L) is near to 2 times than that of the tubes.

5.5. References

Ahvenainen, R., and E. Hurme, "Active and smart packaging for meeting consumer demands for quality and safety, *Food Additives and Contaminants*, 14: 753-763, 1997.

Alnafouri, A.J., and R. Franz, "A study of the equivalence of olive oil and the EU official substitute test media for migration testing at high temperatures," *Food Additives and Contaminants*, 16: 419-431, 1999.

ASTM-D4754-98, Standard Test Method for Two-sided Liquid Extraction of Plastic Materials Using FDA Migration Cell, Vol. 8.03, pp 174-177, 1998

Brody, A.L., E.R. Strupinsky, Kline L. R., *Active Packaging for Food Applications*, Technomic Pub., Lancaster, PV, PP. 12-14, 2001.

De Kruijf, N., M. van Beest, R. Rijk, T. Sipiläinen-Malm, P. Paseiro Losada and B. De Meulenaer, "Active and intelligent packaging: applications and regulatory aspects," *Food Additive and Contaminations*, 19: 144-162, 2002.

Cambridge Encyclopedia, "Acetic acid – Chemical properties, Biochemistry, Production, Applications, Safety," http://encyclopedia.stateuniversity.com/pages/511/acetic-acid.html, (accessed Apr. 15, 2009).

European Commission, "Directive 82/711/EEC of 23 February 1990 relating to plastic materials and articles intended to come into contact with foodstuffs," *Official Journal of the European Communities*, L349, 26-47, 1990.

FDA (U.S. Food and Drug Administration), "Guidance for Industry: Preparation of Food Contact Notification: Administrative, FINAL GUIDANCE" May 2002. http://www.cfsan.fda.gov/~dms/opa2pmna.html#II-B

FDA/CFSAN, Guidance for Industry – Preparation of Premarket Notification, pp.1-38, 2007. www.cfsan.fda.gov/~dms/opa2pmnc.html

Gilbert, J., C. Simoneau, D. Cote and A. Boenke, "An internet compendium of analytical methods and spectroscopic information for monomers and additives used in food packaging plastics," *Food Additives and Contaminants*, 17: 889-893, 2000.

Lopez-Cervantes, J., D.I. Sanchez-Machado, S. Pastorelli, R. Rijk and P. Paseiro-Losada, "Evaluation the migration of ingredients from active packaging and development of dedicated methods: a study of two iron-based oxygen absorbers," *Food additives and contaminants*, 20: 291-299, 2003.

O'Brien, A., A. Goodson and I. Cooper, "Polymer additive migration to foods-a direct comparison of experimental data and values calculated from migration models for high density polyethylene (HDPE)," *Food Additives and Contaminants*, 16: 367-380, 1999.

O'Brien, A., and I. Cooper, "Polymer additive migration to foods-a direct comparison of experimental data and values calculated from migration models for polypropylene," *Food Additives and Contaminants*, 18: 343-355, 2001.

Riquest, A.M., V. Bosc and A. Feigenbaum, "Tailoring fatty food simulants made from solvent mixtures (1): comparison of methanol, ethanol and isopropanol behavior with polystyrene," *Food Additives and Contaminants*, 18: 165-176, 2001.

Smith, J.P., J. Hoshino and Y. Ave, "Interactive packaging involving sachet technology," in M. L, Rooney, ed., *Active Food Packaging*, Blackie Academic & Professional Pub., London, pp. 143-173, 1995.

Teumac, F.N., "The history of oxygen scavenger bottle closure," in M. L, Rooney, ed., *Active Food Packaging*, Blackie Academic & Professional Pub., London, pp. 193-202, 1995.

6. CONCLUSIONS AND FUTURE WORK

6.1. Conclusions

Development of multilayer film incorporating iron based oxygen scavenger was done successfully and the OS2 film was preferred to adopt as an oxygen scavenging film to make an active package, because it did not have agglomerations, and therefore it was superior to OS1 in mechanical properties such as tensile & break strength. For oxygen scavenging, the films were useful even though that had a multilayer structure containing coextruded LLDPE on the inside of the film. The OS2 film was a little better than the OS1, consuming 6.10 cc O_2 per g film after 30 days storage at 23 ℃ and 100% RH.

In the development of active packaging for cosmetics, the active packaging rapidly reduces the oxygen concentration of the headspace compared with conventional packaging. It reached 0.0% from 20.9 % within 30 days and stayed lower than 0.1% for 180 days, while conventional packaging remained near 10.0% after 180 days stored at 23 ℃ and 65% RH. In evaluating the shelf life of retinol in cosmetics, the concentration in the conventional packaging was rapidly reduced from 3,464 IU to 2,511 IU after 24 weeks stored at 23 ℃ and 65% RH, while the concentration in the active packages remained over 3,000 IU after 24 weeks. A shelf life of 51.6 weeks is estimated, based on reduction of retinol to 2,500 IU.

From SEM & EDS analysis, the main elements of oxygen scavenger in the core layer of a multilayer film were identified as iron (Fe), sodium (Na) and chloride (Cl).

Throughout the observation of the migration behavior for the main elements by the SEM & EDS, no migration of any of these main elements was detected in the inner layer adjacent to the core layer containing oxygen scavenger of the OS multilayer films

(OS1 and OS2), which were in direct contact with the food simulants or cosmetic. This means that the main elements of oxygen scavenger in the core layer of the OS films did not pass through the inner layer and did not contact the food simulants and cosmetic. However, from another analysis by SEM & EDS of the seamed parting line in a tube that was stored at 10 days and 40 ℃ in 3% acetic acid, the main elements could be observed, while the main elements were not detected on the non seamed area in the inside of a tube. Therefore, the main elements of oxygen scavenger seem to be migrating through the seamed parting line which was exposed directly to the simulants.

Quantitative analysis of migration of the main elements into various food simulants was conducted using an atomic absorption (AA) spectrometer for both types of oxygen scavengers. For the sums of main migrant components ($NaCl + CaCl_2 + Fe_2O_3$), the migration values in 3% acetic acid were the highest and the next were the values in water among the food simulants. The migration value of OS1 in 3% acetic acid was as 2.322 mg/L, OS2 was 0.928 mg/L and LLDPE was 0.280 mg/L. However, these values are much less than the EU limit for total migration as 60 mg/L (90/128/EEC).

6.2. Future work

The positive effect of an active packaging system to extend the shelf life was observed, and the migration value of main components from oxygen scavenger system was evaluated as smaller than the EU limit. The next step will apply this kind of active packaging system to cosmetics and then pharmaceuticals. However, there are some problems as a future work to reduce the quantity of Si (silicate) and the agglomeration during film and packaging processing and how to protect against the migration from the seamed parting line of the package before commercializing.

Recently, in order to increase the shelf life of products more than ever, oxygen scavengers using nano-composites such as silicate or organo-clay have also been applied. The oxygen scavenger of nano-size may migrate much more easily to products compared with micro-size such as the iron based oxygen scavenger that is currently used. Therefore, this analytical method will be useful in developing this kind of active packaging as another future work.

APPENDICES

APPENDIX A: Properties and oxygen absorbing amount of multilayer film

Table 31. UV/VIS spectrometer data

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
190	13.221	190	16.533	190	56.143
191	11.241	191	23.715	191	59.665
192	21.918	192	5.499	192	71.812
193	17.801	193	16.879	193	54.75
194	4.646	194	1.821	194	33.409
195	-2.158	195	-3.15	195	34.103
196	27.967	196	16.136	196	42.647
197	0.28	197	17.24	197	13.649
198	-5.222	198	19.776	198	7.242
199	1.589	199	20.803	199	7.26
200	20.435	200	27.774	200	4.322
201	-2.587	201	34.642	201	-6.034
202	12.192	202	27.366	202	7.051
203	0.508	203	18.751	203	0.601
204	8.83	204	30.442	204	0.872
205	6.453	205	24.64	205	3.032
206	7.714	206	18.731	206	9.907
207	6.953	207	17.347	207	3.204
208	6.352	208	13.011	208	12.866
209	13.255	209	15.062	209	20.485
210	15.821	210	11.679	210	15.794
211	14.637	211	20.17	211	18.566
212	22.148	212	18.419	212	22.085
213	23.483	213	26.716	213	20.861
214	23.874	214	26.168	214	19.508
215	26.106	215	26.703	215	17.853
216	26.306	216	32.326	216	17.532
217	26.864	217	32.697	217	16.541
218	29.51	218	36.054	218	18.422
219	33.634	219	34.027	219	15.761
220	31.654	220	32.678	220	16.984
221	31.354	221	32.579	221	18.952
222	37.441	222	28.617	222	17.207
223	34.721	223	32.175	223	16.776
224	39.887	224	30.131	224	16.096
225	41.562	225	33.223	225	16.14

Table 31.*(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
226	41.348	226	36.411	226	16.064
227	42.554	227	35.142	227	16.185
228	43.382	228	37.4	228	18.092
229	46.139	229	37.079	229	19.159
230	45.325	230	39.702	230	19.318
231	48.55	231	39.548	231	21.432
232	52.347	232	38.419	232	21.763
233	54.085	233	43.152	233	22.315
234	58.022	234	45.785	234	26.261
235	61.81	235	50.664	235	27.724
236	66.294	236	55.755	236	28.713
237	70.66	237	61.874	237	30.914
238	75.037	238	66.175	238	32.979
239	80.48	239	72.032	239	35.181
240	84.163	240	76.652	240	36.58
241	85.845	241	77.888	241	38.098
242	87.905	242	80.34	242	37.898
243	89.751	243	81.757	243	38.375
244	92.728	244	82.793	244	39.114
245	94.179	245	82.803	245	39.238
246	94.238	246	82.335	246	38.33
247	95.75	247	82.49	247	39.328
248	97.372	248	82.886	248	40.283
249	97.318	249	83.354	249	38.6
250	98.913	250	83.23	250	40.585
251	98.508	251	82.004	251	39.937
252	97.08	252	83.882	252	39.381
253	96.919	253	85.369	253	38.453
254	95.94	254	82.553	254	40.016
255	93.255	255	81.739	255	38.258
256	91.385	256	81.13	256	38.648
257	91.61	257	80.125	257	36.749
258	89.459	258	80.335	258	37.301
259	89.485	259	79.06	259	35.394
260	88.325	260	78.334	260	35.607
261	87.754	261	78.216	261	35.49
262	87.046	262	77.827	262	35.891
263	85.144	263	76.611	263	34.506
264	86.813	264	77.136	264	34.741
265	85.33	265	74.137	265	34.078

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
266	85.822	266	74.164	266	34.06
267	86.58	267	73.971	267	34.657
268	86.28	268	74.086	268	33.424
269	86.459	269	72.268	269	33.785
270	84.555	270	72.097	270	32.74
271	86.167	271	72.389	271	33.594
272	85.352	272	72.788	272	33.362
273	82.971	273	69.424	273	33.052
274	83.991	274	69.06	274	32.446
275	82.244	275	68.92	275	31.155
276	83.922	276	69.413	276	32.838
277	84.112	277	71.285	277	32.43
278	83.792	278	73.205	278	33.661
279	86.049	279	74.639	279	34.389
280	85.97	280	75.419	280	36.199
281	87.277	281	76.445	281	36.09
282	85.519	282	77.713	282	37.343
283	86.934	283	77.095	283	37.719
284	86.939	284	76.932	284	36.06
285	86.51	285	78.72	285	34.943
286	89.315	286	77.86	286	35.795
287	91.291	287	77.262	287	35.537
288	92.793	288	79.024	288	36.107
289	94.034	289	78.517	289	35.434
290	94.204	290	78.935	290	35.693
291	95.079	291	78.663	291	35.542
292	96.171	292	80.023	292	35.531
293	97.173	293	80.147	293	36.439
294	97.778	294	81.859	294	35.763
295	96.353	295	82.827	295	37.424
296	95.488	296	82.718	296	37.302
297	95.335	297	83.076	297	36.933
298	95.607	298	83.207	298	37.375
299	95.158	299	82.887	299	37.387
300	95.378	300	82.699	300	37.8
301	95.288	301	81.3	301	37.548
302	95.231	302	83.047	302	36.769
303	95.421	303	81.078	303	38.689
304	96.159	304	82.437	304	37.67
305	94.962	305	80.514	305	37.369

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
306	95.999	306	80.433	306	37.378
307	94.955	307	80.434	307	37.262
308	94.196	308	78.736	308	36.98
309	94.87	309	78.659	309	36.056
310	95.376	310	79.117	310	35.915
311	94.788	311	78.845	311	34.777
312	93.178	312	79.206	312	35.706
313	93.576	313	79.549	313	35.146
314	93.327	314	82.357	314	35.331
315	93.651	315	81.698	315	35.382
316	95.942	316	82.133	316	35.561
317	94.792	317	83.809	317	35.434
318	96.62	318	82.145	318	35.398
319	96.62	319	82.794	319	35.201
320	96.638	320	83.644	320	36.193
321	95.89	321	83.528	321	36.216
322	94.586	322	80.797	322	35.917
323	95.168	323	81.986	323	36.495
324	93.247	324	80.652	324	35.883
325	93.288	325	79.078	325	36.283
326	93.492	326	78.694	326	35.538
327	93.084	327	78.781	327	35.555
328	91.543	328	87.557	328	41
329	94.692	329	86.049	329	41.896
330	95.972	330	85.391	330	41.136
331	98.004	331	83.184	331	38.818
332	98.566	332	82.425	332	37.955
333	96.461	333	78.62	333	37.088
334	97.893	334	78.049	334	37.179
335	97.484	335	78.265	335	32.061
336	96.693	336	79.744	336	35.272
337	94.764	337	77.475	337	34.737
338	92.642	338	79.214	338	34.905
339	91.339	339	80.353	339	35.376
340	91.419	340	80.115	340	35.999
341	92.083	341	82.566	341	37.296
342	93.458	342	82.025	342	38.597
343	93.866	343	84.137	343	39.354
344	94.859	344	83.874	344	39.345
345	94.901	345	83.661	345	39.694

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
346	93.606	346	82.171	346	40.084
347	93.992	347	80.852	347	39.449
348	93.531	348	81.754	348	38.48
349	92.764	349	79.932	349	36.593
350	94.23	350	80.107	350	36.247
351	93.414	351	81.189	351	35.568
352	95.594	352	82.063	352	36.436
353	96.248	353	81.879	353	38.222
354	96.971	354	81.684	354	38.546
355	95.723	355	82.97	355	38.83
356	96.01	356	81.143	356	39.745
357	98.084	357	82.277	357	39.158
358	94.817	358	81.456	358	38.049
359	94.248	359	79.991	359	38.038
360	94.386	360	80.402	360	36.759
361	92.431	361	79.054	361	36.384
362	91.9	362	79.67	362	35.979
363	92.138	363	78.922	363	36.144
364	92.481	364	78.117	364	35.745
365	91.375	365	79.433	365	35.901
366	92.647	366	77.967	366	35.65
367	93.226	367	77.742	367	36.913
368	93.84	368	78.877	368	35.844
369	94.272	369	79.65	369	36.224
370	94.59	370	79.77	370	36.061
371	95.916	371	79.795	371	36.096
372	94.668	372	79.267	372	36.686
373	95.161	373	79.483	373	35.991
374	95.543	374	79.959	374	36.596
375	93.023	375	80.563	375	36.123
376	94.206	376	79.545	376	36.764
377	95.528	377	80.976	377	35.554
378	93.921	378	81.278	378	37.441
379	95.291	379	82.838	379	37.811
380	92.845	380	81.971	380	37.741
381	92.324	381	81.407	381	37.333
382	95.212	382	81.708	382	36.741
383	91.93	383	79.658	383	34.621
384	92.983	384	78.889	384	36.264
385	93.416	385	79.351	385	36.297

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
386	93.715	386	79.433	386	36.174
387	93.733	387	79.481	387	36.338
388	93.57	388	79.527	388	36.264
389	93.579	389	79.512	389	36.505
390	93.629	390	79.519	390	36.421
391	93.546	391	79.324	391	36.561
392	93.688	392	79.499	392	36.801
393	93.517	393	79.325	393	36.778
394	93.553	394	79.401	394	36.814
395	93.481	395	79.547	395	36.865
396	93.153	396	79.252	396	36.831
397	93.172	397	79.032	397	36.617
398	93.274	398	79.151	398	36.617
399	93.257	399	79.028	399	36.681
400	93.41	400	79.227	400	36.534
401	93.333	401	79.243	401	36.527
402	93.37	402	79.25	402	36.511
403	93.38	403	79.399	403	36.358
404	93.643	404	79.438	404	36.412
405	93.531	405	79.616	405	36.433
406	93.421	406	79.632	406	36.545
407	93.563	407	79.717	407	36.528
408	93.418	408	79.592	408	36.587
409	93.388	409	79.564	409	36.622
410	93.524	410	79.398	410	36.639
411	93.26	411	79.309	411	36.764
412	93.215	412	79.252	412	36.657
413	93.2	413	79.155	413	36.721
414	93.344	414	79.164	414	36.637
415	93.295	415	79.214	415	36.657
416	93.397	416	79.19	416	36.601
417	93.376	417	79.161	417	36.475
418	93.29	418	79.157	418	36.497
419	93.417	419	79.253	419	36.57
420	93.519	420	79.496	420	36.551
421	93.399	421	79.378	421	36.584
422	93.431	422	79.819	422	36.505
423	93.022	423	79.224	423	36.312
424	92.945	424	79.001	424	36.409
425	92.933	425	78.949	425	36.175

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
426	92.765	426	78.766	426	36.235
427	92.918	427	78.947	427	36.204
428	92.821	428	79.051	428	36.23
429	92.872	429	78.817	429	36.562
430	92.983	430	79.093	430	36.603
431	93.081	431	79.393	431	36.661
432	93.231	432	79.312	432	36.934
433	93.101	433	79.228	433	36.726
434	93.359	434	79.556	434	36.893
435	93.203	435	79.524	435	37.076
436	93.119	436	79.554	436	37.024
437	93.451	437	79.624	437	37.058
438	93.406	438	79.688	438	36.949
439	93.51	439	79.643	439	37.025
440	93.743	440	79.626	440	36.971
441	93.538	441	79.683	441	36.773
442	93.416	442	79.691	442	36.814
443	93.429	443	79.648	443	36.599
444	93.426	444	79.519	444	36.587
445	93.409	445	79.471	445	36.668
446	93.304	446	79.342	446	36.715
447	93.523	447	79.308	447	36.593
448	93.238	448	79.363	448	36.55
449	93.241	449	79.262	449	36.769
450	93.167	450	79.343	450	36.812
451	93.109	451	79.274	451	36.746
452	93.027	452	79.274	452	36.857
453	93.029	453	79.312	453	36.821
454	93.019	454	79.168	454	36.896
455	93.1	455	79.241	455	36.799
456	93.095	456	79.241	456	36.813
457	93.391	457	79.507	457	36.643
458	93.285	458	79.428	458	36.745
459	93.385	459	79.415	459	36.734
460	93.417	460	79.578	460	36.732
461	93.475	461	79.657	461	36.762
462	93.406	462	79.7	462	36.919
463	93.396	463	79.66	463	36.935
464	93.275	464	79.723	464	36.999
465	93.139	465	79.73	465	36.995

Table 31.*(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
466	93.195	466	79.587	466	37.032
467	93.219	467	79.814	467	37.046
468	93.188	468	79.668	468	36.969
469	93.176	469	79.564	469	37.112
470	93.16	470	79.571	470	36.955
471	93.324	471	79.506	471	37.091
472	93.347	472	79.347	472	37.07
473	93.208	473	79.432	473	37.025
474	93.325	474	79.463	474	36.988
475	93.397	475	79.47	475	37.024
476	93.38	476	79.474	476	36.952
477	93.325	477	79.627	477	36.98
478	93.219	478	79.587	478	37.057
479	93.329	479	79.774	479	36.961
480	93.319	480	79.813	480	37.037
481	93.289	481	79.635	481	36.985
482	93.296	482	79.815	482	36.975
483	93.221	483	79.806	483	36.939
484	93.213	484	79.784	484	37.066
485	93.21	485	79.646	485	37.076
486	93.164	486	79.604	486	37.006
487	93.307	487	79.662	487	37.183
488	93.24	488	79.742	488	37.176
489	93.314	489	79.764	489	37.156
490	93.211	490	79.685	490	37.147
491	93.207	491	79.622	491	37.183
492	93.268	492	79.657	492	37.295
493	93.255	493	79.765	493	37.304
494	93.274	494	79.741	494	37.306
495	93.289	495	79.83	495	37.21
496	93.159	496	79.678	496	37.178
497	93.176	497	79.71	497	37.082
498	93.253	498	79.793	498	37.172
499	93.356	499	79.876	499	37.188
500	93.36	500	79.941	500	37.09
501	93.382	501	79.938	501	37.335
502	93.436	502	79.924	502	37.267
503	93.401	503	79.962	503	37.29
504	93.406	504	79.985	504	37.345
505	93.455	505	80.041	505	37.413

Table 31.*(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
506	93.315	506	79.994	506	37.402
507	93.253	507	80.001	507	37.394
508	93.208	508	79.935	508	37.433
509	93.364	509	80.009	509	37.348
510	93.278	510	79.867	510	37.484
511	93.226	511	79.944	511	37.489
512	93.295	512	79.947	512	37.448
513	93.238	513	79.876	513	37.447
514	93.285	514	79.852	514	37.41
515	93.258	515	79.912	515	37.355
516	93.218	516	79.877	516	37.34
517	93.222	517	79.892	517	37.335
518	93.265	518	79.875	518	37.307
519	93.174	519	79.936	519	37.268
520	93.24	520	79.966	520	37.315
521	93.331	521	79.945	521	37.336
522	93.201	522	79.987	522	37.289
523	93.205	523	79.978	523	37.339
524	93.289	524	79.871	524	37.399
525	93.252	525	79.918	525	37.414
526	93.201	526	79.838	526	37.45
527	93.311	527	79.855	527	37.544
528	93.367	528	79.972	528	37.519
529	93.281	529	80.033	529	37.523
530	93.222	530	80.001	530	37.533
531	93.239	531	80.19	531	37.601
532	93.216	532	80.239	532	37.654
533	93.07	533	80.15	533	37.634
534	93.275	534	80.18	534	37.627
535	93.211	535	80.17	535	37.618
536	93.272	536	80.151	536	37.602
537	93.19	537	80.001	537	37.558
538	93.257	538	80.111	538	37.577
539	93.191	539	80.022	539	37.511
540	93.232	540	79.968	540	37.552
541	93.16	541	79.926	541	37.545
542	93.155	542	79.99	542	37.54
543	93.242	543	80.008	543	37.73
544	93.248	544	80.044	544	37.636
545	93.236	545	80.073	545	37.731

Table 31.*(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
546	93.15	546	80.084	546	37.719
547	93.148	547	80.056	547	37.714
548	93.114	548	80.064	548	37.711
549	93.18	549	80.195	549	37.751
550	93.152	550	80.158	550	37.789
551	93.216	551	80.213	551	37.802
552	93.151	552	80.116	552	37.834
553	93.387	553	80.122	553	37.808
554	93.31	554	80.215	554	37.776
555	93.238	555	80.184	555	37.793
556	93.245	556	80.144	556	37.828
557	93.25	557	80.219	557	37.775
558	93.124	558	80.195	558	37.811
559	93.152	559	80.314	559	37.915
560	93.121	560	80.21	560	37.939
561	93.169	561	80.222	561	37.924
562	93.172	562	80.291	562	37.874
563	93.125	563	80.214	563	38.023
564	93.114	564	80.067	564	37.935
565	93.056	565	80.102	565	37.959
566	93.192	566	80.1	566	38.009
567	93.241	567	80.17	567	38.009
568	93.163	568	80.208	568	38.078
569	93.168	569	80.179	569	37.984
570	93.184	570	80.2	570	38.006
571	93.289	571	80.252	571	37.98
572	93.171	572	80.238	572	38.033
573	93.127	573	80.389	573	38.103
574	93.228	574	80.386	574	38.025
575	93.23	575	80.388	575	38.075
576	93.247	576	80.415	576	38.036
577	93.337	577	80.466	577	38.124
578	93.293	578	80.388	578	38.092
579	93.296	579	80.402	579	38.057
580	93.341	580	80.334	580	38.129
581	93.271	581	80.296	581	38.05
582	93.216	582	80.23	582	38.069
583	93.137	583	80.145	583	38.109
584	93.303	584	80.241	584	38.1
585	93.039	585	80.118	585	38.14

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
586	93.147	586	80.125	586	38.115
587	93.11	587	80.164	587	38.181
588	93.093	588	80.177	588	38.217
589	93.098	589	80.23	589	38.254
590	93.157	590	80.3	590	38.26
591	93.136	591	80.356	591	38.295
592	93.171	592	80.391	592	38.319
593	93.173	593	80.354	593	38.312
594	93.199	594	80.41	594	38.241
595	93.154	595	80.402	595	38.307
596	93.231	596	80.435	596	38.263
597	93.152	597	80.43	597	38.221
598	93.115	598	80.309	598	38.227
599	93.068	599	80.244	599	38.25
600	93.151	600	80.271	600	38.25
601	93.171	601	80.266	601	38.298
602	93.155	602	80.262	602	38.311
603	93.163	603	80.247	603	38.286
604	93.215	604	80.348	604	38.35
605	93.173	605	80.332	605	38.371
606	93.212	606	80.378	606	38.408
607	93.193	607	80.446	607	38.415
608	93.206	608	80.38	608	38.448
609	93.249	609	80.412	609	38.42
610	93.271	610	80.492	610	38.461
611	93.257	611	80.429	611	38.486
612	93.305	612	80.458	612	38.494
613	93.264	613	80.441	613	38.469
614	93.241	614	80.477	614	38.442
615	93.22	615	80.339	615	38.422
616	93.324	616	80.404	616	38.457
617	93.216	617	80.461	617	38.482
618	93.192	618	80.357	618	38.453
619	93.211	619	80.409	619	38.496
620	93.138	620	80.386	620	38.466
621	93.147	621	80.359	621	38.563
622	93.121	622	80.327	622	38.535
623	93.098	623	80.332	623	38.592
624	93.141	624	80.492	624	38.636
625	93.09	625	80.358	625	38.604

Table 31.*(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
626	93.084	626	80.384	626	38.542
627	93.127	627	80.444	627	38.626
628	93.162	628	80.443	628	38.63
629	93.16	629	80.463	629	38.625
630	93.263	630	80.452	630	38.673
631	93.231	631	80.535	631	38.639
632	93.24	632	80.553	632	38.641
633	93.246	633	80.577	633	38.641
634	93.202	634	80.591	634	38.656
635	93.296	635	80.561	635	38.699
636	93.254	636	80.56	636	38.598
637	93.276	637	80.553	637	38.661
638	93.261	638	80.539	638	38.694
639	93.193	639	80.452	639	38.615
640	93.095	640	80.389	640	38.662
641	93.036	641	80.355	641	38.605
642	93.045	642	80.392	642	38.656
643	93.063	643	80.436	643	38.639
644	93	644	80.494	644	38.72
645	93.049	645	80.489	645	38.705
646	93.079	646	80.638	646	38.799
647	93.11	647	80.566	647	38.87
648	93.095	648	80.578	648	38.84
649	93.203	649	80.72	649	38.866
650	93.179	650	80.647	650	38.871
651	93.136	651	80.605	651	38.904
652	93.08	652	80.54	652	38.896
653	93.107	653	80.513	653	38.914
654	93.151	654	80.527	654	38.856
655	93.043	655	80.389	655	38.954
656	93.143	656	80.46	656	38.913
657	93.034	657	80.41	657	38.836
658	93.145	658	80.423	658	38.784
659	93.129	659	80.478	659	38.894
660	93.101	660	80.428	660	38.845
661	93.151	661	80.477	661	38.787
662	93.14	662	80.567	662	38.831
663	93.176	663	80.555	663	38.865
664	93.143	664	80.524	664	38.912
665	93.165	665	80.51	665	38.938

Table 31.*(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
666	93.164	666	80.577	666	39.03
667	93.183	667	80.677	667	39.02
668	93.199	668	80.644	668	39.03
669	93.275	669	80.717	669	39.026
670	93.197	670	80.718	670	39.101
671	93.273	671	80.718	671	39.134
672	93.249	672	80.763	672	39.151
673	93.299	673	80.711	673	39.108
674	93.26	674	80.69	674	39.089
675	93.124	675	80.573	675	39.008
676	93.135	676	80.601	676	39.047
677	93.181	677	80.653	677	39.081
678	93.229	678	80.571	678	39.05
679	93.106	679	80.556	679	39.053
680	93.149	680	80.654	680	39.041
681	93.122	681	80.646	681	39.082
682	93.042	682	80.664	682	39.023
683	92.996	683	80.549	683	39.065
684	93.069	684	80.686	684	39.033
685	93.055	685	80.716	685	39.101
686	93.135	686	80.636	686	39.165
687	93.185	687	80.579	687	39.161
688	93.137	688	80.545	688	39.178
689	93.154	689	80.603	689	39.203
690	93.138	690	80.617	690	39.213
691	93.173	691	80.637	691	39.243
692	93.108	692	80.689	692	39.224
693	93.139	693	80.696	693	39.251
694	93.109	694	80.763	694	39.239
695	93.171	695	80.788	695	39.229
696	93.134	696	80.822	696	39.289
697	93.1	697	80.771	697	39.219
698	93.153	698	80.726	698	39.213
699	93.141	699	80.665	699	39.243
700	93.13	700	80.624	700	39.188
701	93.122	701	80.55	701	39.156
702	93.113	702	80.588	702	39.229
703	93.135	703	80.592	703	39.167
704	93.141	704	80.614	704	39.215
705	93.119	705	80.666	705	39.22

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
706	93.109	706	80.733	706	39.279
707	93.072	707	80.761	707	39.216
708	93.097	708	80.744	708	39.298
709	93.144	709	80.768	709	39.322
710	93.12	710	80.734	710	39.319
711	93.142	711	80.798	711	39.346
712	93.149	712	80.842	712	39.397
713	93.115	713	80.794	713	39.407
714	93.262	714	80.786	714	39.406
715	93.234	715	80.748	715	39.426
716	93.104	716	80.667	716	39.41
717	93.08	717	80.691	717	39.459
718	93.128	718	80.607	718	39.34
719	93.06	719	80.666	719	39.454
720	93.098	720	80.637	720	39.435
721	93.127	721	80.671	721	39.508
722	93.022	722	80.606	722	39.492
723	93.068	723	80.693	723	39.467
724	93.114	724	80.692	724	39.48
725	93.077	725	80.745	725	39.551
726	93.04	726	80.758	726	39.508
727	93.172	727	80.869	727	39.571
728	93.149	728	80.847	728	39.524
729	93.087	729	80.823	729	39.464
730	93.046	730	80.782	730	39.396
731	93.073	731	80.763	731	39.473
732	93.02	732	80.746	732	39.431
733	93.056	733	80.731	733	39.445
734	93.048	734	80.742	734	39.47
735	93.054	735	80.826	735	39.467
736	93.04	736	80.788	736	39.447
737	93.068	737	80.754	737	39.435
738	93.139	738	80.865	738	39.556
739	93.148	739	80.93	739	39.598
740	93.155	740	80.804	740	39.597
741	93.194	741	80.928	741	39.661
742	93.276	742	80.865	742	39.626
743	93.235	743	80.82	743	39.69
744	93.251	744	80.883	744	39.681
745	93.221	745	80.839	745	39.736

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
746	93.188	746	80.81	746	39.592
747	93.151	747	80.748	747	39.649
748	93.119	748	80.716	748	39.587
749	93.146	749	80.737	749	39.537
750	93.195	750	80.694	750	39.552
751	93.107	751	80.781	751	39.584
752	93.097	752	80.66	752	39.551
753	93.099	753	80.682	753	39.633
754	93.101	754	80.809	754	39.608
755	93.055	755	80.817	755	39.635
756	92.95	756	80.835	756	39.617
757	92.987	757	80.785	757	39.669
758	92.996	758	80.878	758	39.684
759	92.943	759	80.802	759	39.696
760	92.969	760	80.809	760	39.766
761	92.96	761	80.893	761	39.719
762	92.968	762	80.836	762	39.812
763	93.116	763	80.87	763	39.827
764	93.106	764	80.94	764	39.816
765	93.127	765	80.862	765	39.815
766	93.14	766	80.914	766	39.879
767	93.244	767	80.892	767	39.904
768	93.148	768	80.908	768	39.864
769	93.258	769	80.835	769	39.828
770	93.175	770	80.787	770	39.873
771	93.17	771	80.848	771	39.827
772	93.147	772	80.767	772	39.743
773	93.208	773	80.776	773	39.775
774	93.068	774	80.817	774	39.684
775	93.145	775	80.816	775	39.73
776	92.985	776	80.786	776	39.77
777	93.088	777	80.882	777	39.826
778	93.02	778	80.961	778	39.909
779	93.152	779	80.94	779	39.91
780	93.107	780	80.851	780	40.046
781	93.05	781	81.066	781	39.924
782	93.208	782	81.043	782	40.039
783	93.103	783	81.044	783	40.013
784	93.096	784	81.085	784	39.97
785	93.079	785	81.047	785	40.042

Table 31. *(continued)*

LLDPE		OS1		OS2	
nm	Transmittance	nm	Transmittance	nm	Transmittance
786	93.066	786	81.031	786	39.943
787	93.127	787	81.021	787	39.946
788	93.008	788	80.848	788	39.936
789	93.002	789	80.835	789	39.869
790	93.052	790	80.804	790	39.924
791	93.015	791	80.759	791	39.884
792	93.115	792	80.809	792	39.845
793	93.118	793	80.814	793	39.848
794	93.094	794	80.75	794	39.831
795	93.079	795	80.783	795	39.87
796	93.17	796	80.824	796	40.074
797	93.223	797	80.953	797	40.034
798	93.154	798	80.936	798	40.032
799	93.317	799	81.129	799	40.116
800	93.359	800	81.156	800	40.253

Table 32. Film thickness data

1) LLDPE

CD-LLDPE	Sample	1	2	3	4	5
	1	5.5	5.5	5.5	5.0	5.0
	2	5.0	5.5	5.0	5.0	5.5
	3	5.5	5.5	5.5	5.5	5.0
	Ave	5.33	5.50	5.33	5.17	5.17
	Std	0.29	0.00	0.29	0.29	0.29
MD-LLDPE	Sample	1	2	3	4	5
	1	5.5	5.5	5.5	5.5	5.5
	2	5.5	5.5	5.5	5.5	5.0
	3	5.5	5.0	5.5	5.0	5.5
	Avg	5.50	5.33	5.50	5.33	5.33
	Std	0.00	0.29	0.00	0.29	0.29

2) OS1

CD-OS1	Sample	1	2	3	4	5
	1	5.0	4.0	4.5	5.5	5.0
	2	4.5	6.0	5.5	4.0	5.5
	3	5.0	5.0	4.5	5.0	4.5
	Ave	4.83	5.00	4.83	4.83	5.00
	Std	0.29	1.00	0.58	0.76	0.50
MD-OS1	Sample	1	2	3	4	5
	1	4.5	5.5	4.5	5.0	5.5
	2	5.5	4.5	5.5	5.5	5.0
	3	5.0	5.0	5.5	4.5	4.5
	Ave	5.00	5.00	5.17	5.00	5.00
	Std	0.50	0.50	0.58	0.50	0.50

3) OS2

CD-OS2	Sample	1	2	3	4	5
	1	5.0	5.5	5.0	5.5	5.5
	2	5.5	5.0	5.0	5.5	5.0
	3	4.5	5.5	5.0	5.0	5.0
	Ave	5.00	5.33	5.00	5.33	5.17
	Std	0.50	0.29	0.00	0.29	0.29
MD-OS2	Sample	1	2	3	4	5
	1	5.0	5.5	5.0	5.0	5.0
	2	5.0	5.5	5.0	5.0	5.5
	3	5.5	5.0	5.5	5.5	5.0
	Ave	5.17	5.33	5.17	5.17	5.17
	Std	0.29	0.29	0.29	0.29	0.29

Table 33. Mechanical properties data

1) LLDPE

Sample	No.	Maximum Load	Tensile Strength	Break Strength	Break Elongation
		kgf	kg/cm²	kg/cm²	(%)
CD-LLDPE	1	15.22	421.19	374.88	949.9
	2	12.74	352.68	306.31	880.5
	3	13.53	374.38	338.07	913.3
	4	13.77	381.01	343.96	929.2
	5	14.46	400.31	361.39	975.8
	Ave	13.94	385.91	344.92	929.7
	Std	0.941	26.043	26.017	36.14
MD-LLDPE	1	14.00	421.19	374.88	949.9
	2	14.00	352.68	306.31	880.5
	3	14.04	374.38	338.07	913.3
	4	13.94	371.93	336.07	907.3
	5	14.12	376.85	340.29	918.7
	Ave	14.02	379.41	339.13	913.9
	Std	0.065	25.237	24.327	24.89

2) OS1

Sample	No.	Maximum Load	Tensile Strength	Break Strength	Break Elongation
		kgf	kg/cm²	kg/cm²	(%)
CD-OS1	1	6.56	217.32	163.87	681.3
	2	6.84	226.49	181.97	705.3
	3	7.20	238.39	238.39	704.6
	4	7.06	233.82	181.54	707.7
	5	6.91	228.71	183.79	705.2
	Ave	6.91	228.95	189.91	700.8
	Std	0.241	7.969	28.279	10.98
MD-OS1	1	7.88	260.91	211.55	609.7
	2	7.80	244.86	192.91	614.3
	3	7.29	228.19	179.98	630.2
	4	7.43	232.98	186.44	605.4
	5	7.72	242.07	201.21	601.8
	Ave	7.62	241.80	194.42	612.3
	Std	0.253	12.626	12.390	11.06

3) OS2

Sample	No.	Maximum Load	Tensile Strength	Break Strength	Break Elongation
		kgf	kg/cm²	kg/cm²	(%)
CD-OS2	1	8.97	267.43	222.55	761
	2	9.35	278.76	237.09	777.4
	3	8.08	242.06	199.99	724.6
	4	8.87	264.26	217.20	764.3
	5	8.74	260.52	220.87	768.5
	Ave	8.80	262.61	219.54	759.2
	Std	0.463	13.355	13.291	20.27
MD-OS2	1	9.46	293.14	240.91	694.1
	2	9.72	301.27	256.41	699.6
	3	10.85	336.29	294.08	732.1
	4	10.14	314.21	270.71	704.1
	5	9.91	303.81	258.55	706.4
	Ave	10.01	309.74	264.13	707.3
	Std	0.529	16.640	19.814	14.66

Table 34. Oxygen absorbing amount data

1) The value of 50 % - OS1 and OS2

Film	SAMPLE	0 DAY	30 DAYS	O2 Absorb	FILM WT	O2 Absorb
OS1-	No.	(cc)	(cc)	(cc)	(g)	(cc/g)
50%	1	205.0	183.1	21.9	3.99	5.49
	2	198.3	175.2	23.1	4.01	5.76
	3	201.2	177.9	23.3	4.02	5.80
	Ave	201.5	178.7	22.8	4.01	5.68
	Std	3.36	4.02	0.76	0.02	0.17
OS2-	1	199.8	175.2	24.6	4.01	6.13
50%	2	202.5	178.2	24.3	3.97	6.12
	3	203.3	179.1	24.2	4.01	6.03
	Ave	201.9	177.5	24.4	4.00	6.10
	Std	1.83	2.04	0.21	0.02	0.05

2) The value of 20 %, 30 %, 50 % - OS1 and OS2

Film	OS Content	0 Day	0 Day	30 Day	30 Day	O2 Absorb	Film Wt.	O2 Absorb	O2 Absorb Content
	(%)	(cc)	(%)	(cc)	(%)	(cc)	(g)	(cc/g)	(%)
OS1	*50	201.5	20.9	178.7	18.5	22.8	4.01	5.68	50.7
	30	199.1	20.9	189.0	19.8	10.1	3.01	3.36	29.9
	20	205.0	20.9	198.3	20.2	6.7	2.99	2.24	20.0
OS2	*50	201.9	20.9	177.5	18.4	24.4	4.00	6.10	50.4
	30	199.3	20.9	188.4	19.8	10.9	3.00	3.63	30.1
	20	203.3	20.9	196.0	20.1	7.3	3.02	2.42	20.0

*50: Average of three specimens of OS1 - 50% and OS2 - 50 % on Table 22 – 1

APPENDIX B: Oxygen and retinol concentration of active packaging

Table 35. Oxygen concentration in headspace data

Day	0	7	30	60	90	120	150	180
Control	20.060	16.750	12.500	10.570	10.020	9.780	9.520	9.290
	20.200	17.020	13.200	11.080	10.430	10.120	9.770	9.520
	19.950	16.280	12.030	10.240	9.750	9.470	9.220	9.050
Ave	20.070	16.683	12.577	10.630	10.067	9.790	9.503	9.287
Std	0.125	0.374	0.589	0.423	0.342	0.325	0.275	0.235
OS2	20.120	2.980	0.000	0.000	0.000	0.000	0.000	0.010
	20.240	4.020	0.000	0.000	0.000	0.000	0.020	0.000
	20.000	3.250	0.000	0.000	0.000	0.000	0.000	0.020
Ave	20.120	3.417	0.000	0.000	0.000	0.000	0.007	0.010
Std	0.120	0.540	0.000	0.000	0.000	0.000	0.012	0.010

Table 36. Standard calibration curve data

Unit: AU

Sample	0.1mg/100ml	0.4mg/100ml	1mg/100ml	3mg/100ml
1	1,225	5,543	11,983	32,923
2	1,273	5,922	13,427	34,477
3	1,349	5,471	12,245	36,647
4	1,309	5,884	12,649	33,896
Ave	1,289	5,705	12,576	34,486
Std	52.8	231.0	630.0	1577.0
Error rate (%)	4.093	4.050	5.010	4.573

$$\text{Error rate (\%)} = \frac{Std}{Ave} \times 100$$

Table 37. Area Response data of retinol in HPLC

Unit: AU

Sample	No.	1 week	2 weeks	4 weeks	8 weeks	12 week	24 week
OS	1	24,505	24,261	24,031	23,246	22,243	21,140
	2	24,112	23,787	23,544	22,758	21,959	20,937
	3	24,898	24,647	24,356	23,604	22,711	21,709
	Ave	24,505	24,232	23,977	23,203	22,304	21,262
	Std	393	431	409	425	380	400
Control	1	23,835	23,036	22,365	22,122	19,874	17,490
	2	24,370	23,503	22,860	22,589	20,469	17,937
	3	24,627	23,787	23,151	23,015	20,327	18,039
	Ave	24,277	23,442	22,792	22,575	20,223	17,822
	Std	404	379	397	447	311	292

Table 38. Retinol concentration data in cosmetics

1) mg/100 ml

Unit: mg/100 ml

Sample	No.	1 week	2 weeks	4 weeks	8 weeks	12 week	24 week
OS	1	2.10	2.08	2.06	1.99	1.90	1.80
	2	2.06	2.04	2.01	1.94	1.87	1.78
	3	2.13	2.11	2.09	2.02	1.94	1.85
	Ave	2.10	2.07	2.05	1.98	1.90	1.81
	Std	0.03	0.04	0.04	0.04	0.03	0.04
Control	1	2.04	1.97	1.91	1.89	1.69	1.48
	2	2.09	2.01	1.95	1.93	1.74	1.52
	3	2.11	2.04	1.98	1.97	1.73	1.53
	Ave	2.08	2.00	1.95	1.93	1.72	1.51
	Std	0.04	0.03	0.04	0.04	0.03	0.03

From the standard curve,

$$Y = 11284X + 819.79$$

$$X = \frac{Y - 819.79}{11284}$$

where, X: Retinol concentration (mg/100 ml)

Y: Area Response of retinol in HPLC

2) IU/g

Unit: IU/g

Sample	No.	1 week	2 weeks	4 weeks	8 weeks	12 week	24 week
OS	1	3,498	3,462	3,428	3,312	3,164	3,001
	2	3,440	3,392	3,356	3,240	3,122	2,971
	3	3,556	3,519	3,476	3,365	3,233	3,085
	Ave	3,498	3,458	3,420	3,306	3,173	3,019
	Std	58	64	60	63	56	59
Control	1	3,399	3,281	3,182	3,146	2,814	2,462
	2	3,478	3,350	3,255	3,215	2,902	2,528
	3	3,516	3,392	3,298	3,278	2.881	2,543
	Ave	3,464	3,341	3,245	3,213	2,866	2,511
	Std	60	56	59	66	46	43

If a retinol concentration is X (mg/100 ml),

$$X = \frac{2 \times C(IU/g)}{3333(IU/mg)}$$

$$C = \frac{X \times 3333(IU/mg)}{2}$$

where, C: Retinol concentration (IU/g)

1 mg retinol = 3333 IU, 1 IU = 0.300 μg

APPENDIX C: Migration data into various food simulants

Table 39. Standard calibration curve data of Na for 95 % ethanol in AA

ppm	Abs	Ave Abs
0	0.0051	0.00340
	0.0033	
	0.0018	
1	0.1278	0.11967
	0.1178	
	0.1134	
3	0.3465	0.34767
	0.3473	
	0.3492	
5	0.5577	0.55540
	0.5554	
	0.5531	
8	0.9418	0.93917
	0.9372	
	0.9385	
10	1.1002	1.07017
	1.1014	
	1.0089	

Table 40. Standard calibration curve data of Na for water and 3 % acetic acid in AA

ppm	Abs	Ave Abs
0	0.0044	0.00830
	0.0113	
	0.0092	
1	0.8524	0.85787
	0.8457	
	0.8755	
3	1.7301	1.73140
	1.7211	
	1.7430	
5	2.6479	2.62223
	2.6044	
	2.6144	
10	4.2305	4.19513
	4.1864	
	4.1685	
15	6.4023	6.41267
	6.4025	
	6.4332	
20	8.4421	8.33853
	8.3321	
	8.2414	

Table 41. Standard calibration curve data of Na for olive oil in AA

ppm	Abs	Ave Abs
0	0.0816	0.05880
	0.0578	
	0.0370	
1	0.4272	0.42623
	0.4275	
	0.4240	
3	0.6252	0.67263
	0.6926	
	0.7001	
5	1.2936	1.33093
	1.3866	
	1.3126	

Table 42. Standard calibration curve data of Ca for 95 % ethanol in AA

ppm	Abs	Ave Abs
0	0.0028	0.00287
0	0.0010	
0	0.0048	
1	0.4511	0.44610
1	0.4456	
1	0.4416	
3	0.9301	0.92230
3	0.9217	
3	0.9151	
5	1.5265	1.51003
5	1.5098	
5	1.4938	
8	2.2413	2.22087
8	2.2119	
8	2.2094	
10	2.7070	2.68173
10	2.6802	
10	2.6580	

Table 43. Standard calibration curve data of Ca for water and 3 % acetic acid in AA

ppm	Abs	Ave Abs
0	0.0057	0.00333
	0.0034	
	0.0009	
1	0.1269	0.12827
	0.1306	
	0.1273	
3	0.3448	0.34650
	0.3473	
	0.3474	
5	0.5577	0.55533
	0.5558	
	0.5525	
8	0.9434	0.94200
	0.9441	
	0.9385	
10	1.1052	1.10160
	1.1007	
	1.0989	

Table 44. Standard calibration curve data of Ca for olive oil in AA

ppm	Abs	Ave Abs
0	0.0021	0.00313
	0.0051	
	0.0022	
1	0.0541	0.05693
	0.0612	
	0.0555	
3	0.0955	0.09323
	0.0899	
	0.0943	
5	0.1241	0.129067
	0.1342	
	0.1289	

Table 45. Standard calibration curve data of Fe for 95 % ethanol in AA

ppm	Abs	Ave Abs
0	0.0001	0.00073
	0.0007	
	0.0014	
1	0.1367	0.13953
	0.1407	
	0.1412	
2	0.3140	0.31260
	0.3111	
	0.3127	
3	0.3650	0.36923
	0.3657	
	0.3770	
5	0.7964	0.79817
	0.7991	
	0.7990	
10	1.5557	1.55873
	1.5552	
	1.5653	
20	3.1302	3.11773
	3.1021	
	3.1209	

Table 46. Standard calibration curve data of Fe for water and 3 % acetic acid in AA

ppm	Abs	Ave Abs
0	0.0029	0.00480
	0.0064	
	0.0051	
1	0.0885	0.09010
	0.0898	
	0.0920	
2	0.1941	0.19330
	0.1934	
	0.1924	
3	0.2935	0.29513
	0.2954	
	0.2965	
5	0.4855	0.48750
	0.4872	
	0.4898	
10	0.9391	0.94200
	0.9401	
	0.9468	
20	1.8915	1.89677
	1.9113	
	1.8875	

Table 47. Standard calibration curve data of Fe for olive oil in AA

ppm	Abs	Ave Abs
0	0.0099	0.00877
	0.0087	
	0.0077	
1	0.0170	0.01713
	0.0184	
	0.0160	
3	0.0712	0.07127
	0.0685	
	0.0741	
5	0.1098	0.11453
	0.1222	
	0.1116	

Table 48. Migration of NaCl into 95 % ethanol as calculated from observed migration of sodium (Na), respectively

	Sample #	Na μg/30ml	NaCl μg/30ml	NaCl mg/L	Ave	Std
OS1	1	3.54	9.01	0.30	0.300	0.000
	1	3.54	8.99	0.30		
	1	3.54	9.00	0.30		
	2	3.42	8.70	0.29	8.663	0.001
	2	3.41	8.66	0.29		
	2	3.40	8.63	0.29		
	3	3.27	8.31	0.28	8.344	0.001
	3	3.28	8.34	0.28		
	3	3.30	8.38	0.28		
	4	3.74	9.50	0.32	9.457	0.002
	4	3.73	9.47	0.32		
	4	3.70	9.41	0.31		
OS2	1	1.24	3.14	0.10	3.111	0.001
	1	1.22	3.11	0.10		
	1	1.21	3.09	0.10		
	2	1.15	2.92	0.10	2.920	0.000
	2	1.15	2.93	0.10		
	2	1.14	2.91	0.10		
	3	1.35	3.42	0.11	3.405	0.001
	3	1.34	3.40	0.11		
	3	1.33	3.39	0.11		
	4	1.08	2.75	0.09	2.750	0.001
	4	1.09	2.78	0.09		
	4	1.07	2.72	0.09		
LLDPE	1	0.60	1.52	0.05	1.553	0.001
	1	0.62	1.56	0.05		
	1	0.62	1.58	0.05		
	2	0.58	1.48	0.05	1.430	0.001
	2	0.55	1.41	0.05		
	2	0.55	1.40	0.05		
	3	0.49	1.25	0.04	1.223	0.001
	3	0.47	1.19	0.04		
	3	0.48	1.22	0.04		
	4	0.42	1.06	0.04	1.091	0.001
	4	0.44	1.13	0.04		
	4	0.43	1.09	0.04		

Table 49. Migration of NaCl into water as calculated from observed migration of sodium (Na), respectively

	Sample #	Na μg/30ml	NaCl μg/30ml	NaCl mg/L	Ave	Std
OS1	1	17.95	45.60	1.52	1.526	0.005
	1	18.01	45.77	1.53		
	1	18.07	45.92	1.53		
	2	17.85	45.35	1.51	1.510	0.003
	2	17.79	45.20	1.51		
	2	17.86	45.39	1.51		
	3	17.96	45.64	1.52	1.518	0.008
	3	17.82	45.27	1.51		
	3	17.99	45.70	1.52		
	4	17.47	44.38	1.48	1.478	0.001
	4	17.44	44.31	1.48		
	4	17.45	44.33	1.48		
OS2	1	3.40	8.63	0.29	0.290	0.002
	1	3.44	8.74	0.29		
	1	3.42	8.70	0.29		
	2	3.97	10.09	0.34	0.333	0.003
	2	3.90	9.90	0.33		
	2	3.93	9.97	0.33		
	3	3.35	8.52	0.28	0.282	0.002
	3	3.34	8.48	0.28		
	3	3.31	8.42	0.28		
	4	3.70	9.41	0.31	0.317	0.003
	4	3.76	9.55	0.32		
	4	3.77	9.58	0.32		
LLDPE	1	2.12	5.39	0.18	0.183	0.003
	1	2.15	5.47	0.18		
	1	2.20	5.59	0.19		
	2	2.52	6.39	0.21	0.204	0.008
	2	2.36	6.00	0.20		
	2	2.35	5.97	0.20		
	3	2.07	5.25	0.18	0.176	0.001
	3	2.09	5.31	0.18		
	3	2.07	5.25	0.17		
	4	1.95	4.94	0.16	0.164	0.001
	4	1.93	4.91	0.16		
	4	1.93	4.90	0.16		

Table 50. Migration of NaCl into 3 % acetic acid as calculated from observed migration of sodium (Na), respectively

	Sample #	Na μg/30ml	NaCl μg/30ml	NaCl mg/L	Ave	Std
OS1	1	16.84	42.79	1.43	1.430	0.005
	1	16.87	42.86	1.43		
	1	16.96	43.09	1.44		
	2	17.38	44.15	1.47	1.473	0.006
	2	17.32	44.02	1.47		
	2	17.47	44.40	1.48		
	3	17.92	45.53	1.52	1.518	0.001
	3	17.93	45.56	1.52		
	3	17.92	45.52	1.52		
	4	17.46	44.35	1.48	1.476	0.003
	4	17.44	44.32	1.48		
	4	17.39	44.18	1.47		
OS2	1	4.25	10.79	0.36	0.366	0.007
	1	4.31	10.95	0.36		
	1	4.41	11.21	0.37		
	2	4.32	10.97	0.37	0.373	0.018
	2	4.65	11.82	0.39		
	2	4.26	10.82	0.36		
	3	4.57	11.62	0.39	0.374	0.011
	3	4.33	11.00	0.37		
	3	4.35	11.06	0.37		
	4	3.84	9.76	0.33	0.334	0.010
	4	3.91	9.93	0.33		
	4	4.07	10.35	0.35		
LLDPE	1	2.83	7.20	0.24	0.243	0.003
	1	2.87	7.29	0.24		
	1	2.89	7.35	0.24		
	2	2.68	6.80	0.23	0.230	0.004
	2	2.71	6.90	0.23		
	2	2.77	7.03	0.23		
	3	3.23	8.20	0.27	0.270	0.003
	3	3.15	7.99	0.27		
	3	3.18	8.08	0.27		
	4	2.45	6.22	0.21	0.216	0.008
	4	2.62	6.67	0.22		
	4	2.59	6.58	0.22		

Table 51. Migration of NaCl into olive oil as calculated from observed migration of sodium (Na), respectively

	Sample #	Na μg/30ml	NaCl μg/30ml	NaCl mg/L	Ave	Std
OS1	1	0.57	1.45	0.05	1.317	0.219
	1	0.57	1.44	0.05		
	1	0.42	1.06	0.04		
	2	0.39	1.00	0.03	1.355	0.331
	2	0.56	1.42	0.05		
	2	0.65	1.65	0.05		
	3	0.01	0.04	0.00	1.046	0.878
	3	0.59	1.50	0.05		
	3	0.63	1.61	0.05		
	4	0.59	1.51	0.05	1.332	1.085
	4	0.07	0.17	0.01		
	4	0.91	2.32	0.08		
OS2	1	0.38	0.98	0.03	1.055	0.099
	1	0.40	1.02	0.03		
	1	0.46	1.17	0.04		
	2	0.46	1.17	0.04	1.301	0.178
	2	0.59	1.50	0.05		
	2	0.49	1.23	0.04		
	3	0.40	1.01	0.03	1.026	0.017
	3	0.40	1.02	0.03		
	3	0.41	1.05	0.03		
	4	0.40	1.01	0.03	0.961	0.059
	4	0.38	0.97	0.03		
	4	0.35	0.90	0.03		
LLDPE	1	0.50	1.28	0.04	1.207	0.109
	1	0.50	1.26	0.04		
	1	0.43	1.08	0.04		
	2	0.34	0.86	0.03	0.923	0.076
	2	0.35	0.90	0.03		
	2	0.40	1.01	0.03		
	3	0.36	0.91	0.03	1.167	0.386
	3	0.39	0.98	0.03		
	3	0.63	1.61	0.05		
	4	0.69	1.75	0.06	1.921	0.750
	4	1.08	2.74	0.09		
	4	0.50	1.27	0.04		

Table 52. Migration of $CaCl_2$ into 95 % ethanol as calculated from observed migration of calcium (Ca), respectively

	Sample #	Ca μg/30ml	$CaCl_2$ μg/30ml	$CaCl_2$ mg/L	Ave	Std
OS1	1	-0.38	-1.07	-0.04	-0.036	0.000
	1	-0.39	-1.09	-0.04		
	1	-0.39	-1.07	-0.04		
	2	-0.39	-1.09	-0.04	-0.036	0.001
	2	-0.40	-1.10	-0.04		
	2	-0.38	-1.05	-0.03		
	3	-0.38	-1.05	-0.04	-0.035	0.001
	3	-0.38	-1.06	-0.04		
	3	-0.36	-1.01	-0.03		
	4	-0.37	-1.03	-0.03	-0.035	0.001
	4	-0.36	-1.01	-0.03		
	4	-0.39	-1.09	-0.04		
OS2	1	-0.37	-1.01	-0.03	-0.035	0.001
	1	-0.38	-1.06	-0.04		
	1	-0.39	-1.07	-0.04		
	2	-0.37	-1.02	-0.03	-0.035	0.001
	2	-0.38	-1.06	-0.04		
	2	-0.37	-1.04	-0.03		
	3	-0.36	-1.01	-0.03	-0.034	0.001
	3	-0.38	-1.05	-0.03		
	3	-0.36	-1.00	-0.03		
	4	-0.37	-1.02	-0.03	-0.034	0.000
	4	-0.36	-1.00	-0.03		
	4	-0.36	-1.00	-0.03		
LLDPE	1	-0.34	-0.95	-0.03	-0.032	0.001
	1	-0.36	-0.99	-0.03		
	1	-0.34	-0.94	-0.03		
	2	-0.33	-0.93	-0.03	-0.032	0.001
	2	-0.35	-0.97	-0.03		
	2	-0.35	-0.96	-0.03		
	3	-0.34	-0.96	-0.03	-0.032	0.001
	3	-0.36	-0.99	-0.03		
	3	-0.34	-0.95	-0.03		
	4	-0.34	-0.95	-0.03	-0.031	0.001
	4	-0.32	-0.89	-0.03		
	4	-0.34	-0.93	-0.03		

Table 53. Migration of $CaCl_2$ into water as calculated from observed migration of calcium (Ca), respectively

	Sample #	Ca μg/30ml	$CaCl_2$ μg/30ml	$CaCl_2$ mg/L	Ave	Std
OS1	1	0.04	0.12	0.00	0.001	0.002
	1	0.00	0.00	0.00		
	1	0.00	0.00	0.00		
	2	0.06	0.18	0.01	0.002	0.003
	2	0.00	0.00	0.00		
	2	0.00	0.00	0.00		
	3	0.05	0.13	0.00	0.001	0.003
	3	0.00	0.00	0.00		
	3	0.00	0.00	0.00		
	4	0.04	0.11	0.00	0.001	0.002
	4	0.00	0.00	0.00		
	4	0.00	0.00	0.00		
OS2	1	0.40	1.11	0.04	0.012	0.021
	1	0.00	0.00	0.00		
	1	0.00	0.00	0.00		
	2	0.58	1.62	0.05	0.018	0.031
	2	0.00	0.00	0.00		
	2	0.00	0.00	0.00		
	3	0.40	1.11	0.04	0.012	0.021
	3	0.00	0.00	0.00		
	3	0.00	0.00	0.00		
	4	1.14	3.16	0.11	0.035	0.061
	4	0.00	0.00	0.00		
	4	0.00	0.00	0.00		
LLDPE	1	0.21	0.59	0.02	0.007	0.011
	1	0.00	0.00	0.00		
	1	0.00	0.00	0.00		
	2	0.27	0.76	0.03	0.008	0.015
	2	0.00	0.00	0.00		
	2	0.00	0.00	0.00		
	3	0.23	0.63	0.02	0.007	0.012
	3	0.00	0.00	0.00		
	3	0.00	0.00	0.00		
	4	0.48	1.33	0.04	0.015	0.026
	4	0.00	0.00	0.00		
	4	0.00	0.00	0.00		

Table 54. Migration of $CaCl_2$ into 3 % acetic acid as calculated from observed migration of calcium (Ca), respectively

	Sample #	Ca μg/30ml	$CaCl_2$ μg/30ml	$CaCl_2$ mg/L	Ave	Std
OS1	1	0.27	0.75	0.02	0.025	0.000
	1	0.27	0.76	0.03		
	1	0.28	0.76	0.03		
	2	0.32	0.89	0.03	0.031	0.001
	2	0.35	0.97	0.03		
	2	0.32	0.90	0.03		
	3	0.35	0.98	0.03	0.031	0.001
	3	0.34	0.94	0.03		
	3	0.32	0.90	0.03		
	4	0.27	0.76	0.03	0.024	0.002
	4	0.24	0.67	0.02		
	4	0.27	0.76	0.03		
OS2	1	4.95	13.74	0.46	0.457	0.001
	1	4.93	13.69	0.46		
	1	4.95	13.72	0.46		
	2	4.47	12.39	0.41	0.405	0.009
	2	4.28	11.87	0.40		
	2	4.39	12.17	0.41		
	3	4.27	11.84	0.39	0.420	0.047
	3	5.13	14.23	0.47		
	3	4.24	11.77	0.39		
	4	4.17	11.57	0.39	0.156	0.001
	4	4.09	11.34	0.38		
	4	4.24	11.76	0.39		
LLDPE	1	0.37	1.03	0.03	0.035	0.001
	1	0.39	1.08	0.04		
	1	0.37	1.03	0.03		
	2	0.42	1.17	0.04	0.042	0.004
	2	0.50	1.38	0.05		
	2	0.43	1.18	0.04		
	3	0.33	0.92	0.03	0.031	0.002
	3	0.30	0.85	0.03		
	3	0.36	0.99	0.03		
	4	0.15	0.43	0.01	0.014	0.001
	4	0.14	0.38	0.01		
	4	0.15	0.42	0.01		

Table 55. Migration of $CaCl_2$ into olive oil as calculated from observed migration of calcium (Ca), respectively

	Sample #	Ca μg/30ml	$CaCl_2$ μg/30ml	$CaCl_2$ mg/L	Ave	Std
OS1	1	-0.41	-1.13	-0.04	0.022	0.053
	1	0.43	1.19	0.04		
	1	0.70	1.93	0.06		
	2	1.49	4.15	0.14	0.070	0.059
	2	0.32	0.88	0.03		
	2	0.47	1.31	0.04		
	3	0.81	2.26	0.08	0.036	0.041
	3	-0.06	-0.18	-0.01		
	3	0.43	1.19	0.04		
	4	0.85	2.36	0.08	0.053	0.022
	4	0.40	1.12	0.04		
	4	0.47	1.31	0.04		
OS2	1	1.29	3.57	0.12	0.117	0.002
	1	1.25	3.47	0.12		
	1	1.27	3.51	0.12		
	2	-0.06	-0.18	-0.01	0.086	0.081
	2	1.27	3.53	0.12		
	2	1.59	4.41	0.15		
	3	2.01	5.57	0.19	0.176	0.019
	3	1.66	4.60	0.15		
	3	2.03	5.62	0.19		
	4	1.70	4.73	0.16	0.109	0.042
	4	0.87	2.41	0.08		
	4	0.98	2.71	0.09		
LLDPE	1	1.08	3.00	0.10	0.060	0.035
	1	0.41	1.13	0.04		
	1	0.45	1.24	0.04		
	2	0.61	1.70	0.06	0.037	0.025
	2	0.50	1.38	0.05		
	2	0.09	0.25	0.01		
	3	0.60	1.66	0.06	0.037	0.016
	3	0.27	0.75	0.02		
	3	0.32	0.90	0.03		
	4	0.39	1.07	0.04	0.046	0.017
	4	0.39	1.07	0.04		
	4	0.71	1.96	0.07		

Table 56. Migration of Fe_2O_3 into 95 % ethanol as calculated from observed migration of iron (Fe), respectively

	Sample #	Fe μg/30ml	Fe_2O_3 μg/30ml	Fe_2O_3 mg/L	Ave	Std
OS1	1	0.15	0.21	0.01	0.007	0.000
	1	0.13	0.19	0.01		
	1	0.14	0.19	0.01		
	2	0.15	0.21	0.01	0.006	0.000
	2	0.13	0.18	0.01		
	2	0.13	0.19	0.01		
	3	0.13	0.19	0.01	0.007	0.000
	3	0.15	0.21	0.01		
	3	0.14	0.20	0.01		
	4	0.13	0.19	0.01	0.006	0.000
	4	0.13	0.18	0.01		
	4	0.13	0.18	0.01		
OS2	1	0.14	0.19	0.01	0.007	0.001
	1	0.16	0.23	0.01		
	1	0.13	0.19	0.01		
	2	0.15	0.22	0.01	0.007	0.000
	2	0.13	0.19	0.01		
	2	0.14	0.20	0.01		
	3	0.13	0.19	0.01	0.006	0.000
	3	0.13	0.18	0.01		
	3	0.13	0.19	0.01		
	4	0.14	0.20	0.01	0.007	0.000
	4	0.14	0.20	0.01		
	4	0.13	0.19	0.01		
LLDPE	1	0.14	0.19	0.01	0.007	0.000
	1	0.15	0.22	0.01		
	1	0.14	0.19	0.01		
	2	0.14	0.20	0.01	0.007	0.000
	2	0.15	0.21	0.01		
	2	0.15	0.21	0.01		
	3	0.14	0.21	0.01	0.007	0.000
	3	0.14	0.20	0.01		
	3	0.16	0.23	0.01		
	4	0.14	0.20	0.01	0.007	0.000
	4	0.14	0.20	0.01		
	4	0.13	0.19	0.01		

Table 57. Migration of Fe_2O_3 into water as calculated from observed migration of iron (Fe), respectively

	Sample #	Fe μg/30ml	Fe_2O_3 μg/30ml	Fe_2O_3 mg/L	Ave	Std
OS1	1	2.18	3.12	0.10	0.035	0.060
	1	0.00	0.00	0.00		
	1	0.00	0.00	0.00		
	2	1.54	2.20	0.07	0.024	0.042
	2	0.00	0.00	0.00		
	2	0.00	0.00	0.00		
	3	1.87	2.68	0.09	0.030	0.052
	3	0.00	0.00	0.00		
	3	0.00	0.00	0.00		
	4	1.65	2.36	0.08	0.026	0.045
	4	0.00	0.00	0.00		
	4	0.00	0.00	0.00		
OS2	1	0.00	0.00	0.00	0.000	0.000
	1	0.00	0.00	0.00		
	1	0.00	0.00	0.00		
	2	-0.03	-0.04	0.00	0.000	0.001
	2	0.00	0.00	0.00		
	2	0.00	0.00	0.00		
	3	0.00	0.00	0.00	0.000	0.000
	3	0.00	0.00	0.00		
	3	0.00	0.00	0.00		
	4	0.01	0.01	0.00	0.000	0.000
	4	0.00	0.00	0.00		
	4	0.00	0.00	0.00		
LLDPE	1	-0.01	-0.01	0.00	0.000	0.000
	1	0.00	0.00	0.00		
	1	0.00	0.00	0.00		
	2	-0.02	-0.02	0.00	0.000	0.000
	2	0.00	0.00	0.00		
	2	0.00	0.00	0.00		
	3	-0.02	-0.02	0.00	0.000	0.000
	3	0.00	0.00	0.00		
	3	0.00	0.00	0.00		
	4	-0.03	-0.05	0.00	-0.001	0.001
	4	0.00	0.00	0.00		
	4	0.00	0.00	0.00		

Table 58. Migration of Fe_2O_3 into 3 % acetic acid as calculated from observed migration of iron (Fe), respectively

	Sample #	Fe μg/30ml	Fe_2O_3 μg/30ml	Fe_2O_3 mg/L	Ave	Std
OS1	1	19.79	28.29	0.94	0.945	0.002
	1	19.86	28.40	0.95		
	1	19.84	28.37	0.95		
	2	15.47	22.11	0.74	0.736	0.001
	2	15.41	22.04	0.73		
	2	15.43	22.06	0.74		
	3	16.17	23.12	0.77	0.772	0.001
	3	16.19	23.14	0.77		
	3	16.22	23.19	0.77		
	4	17.28	24.70	0.82	0.822	0.002
	4	17.25	24.66	0.82		
	4	17.20	24.59	0.82		
OS2	1	2.93	4.19	0.14	0.140	0.001
	1	2.93	4.19	0.14		
	1	2.98	4.26	0.14		
	2	3.09	4.42	0.15	0.146	0.001
	2	3.06	4.37	0.15		
	2	3.06	4.38	0.15		
	3	2.92	4.18	0.14	0.140	0.001
	3	2.93	4.19	0.14		
	3	2.96	4.23	0.14		
	4	3.33	4.76	0.16	0.159	0.001
	4	3.35	4.79	0.16		
	4	3.33	4.76	0.16		
LLDPE	1	0.34	0.49	0.02	0.015	0.001
	1	0.29	0.42	0.01		
	1	0.32	0.45	0.02		
	2	0.31	0.44	0.01	0.014	0.001
	2	0.29	0.41	0.01		
	2	0.28	0.40	0.01		
	3	0.31	0.44	0.01	0.014	0.001
	3	0.30	0.42	0.01		
	3	0.27	0.38	0.01		
	4	0.28	0.40	0.01	0.013	0.001
	4	0.29	0.41	0.01		
	4	0.27	0.38	0.01		

Table 59. Migration of Fe_2O_3 into olive oil as calculated from observed migration of iron (Fe), respectively

	Sample #	Fe μg/30ml	Fe_2O_3 μg/30ml	Fe_2O_3 mg/L	Ave	Std
OS1	1	0.32	0.46	0.02	0.006	0.014
	1	-0.21	-0.29	-0.01		
	1	0.25	0.36	0.01		
	2	0.18	0.26	0.01	0.005	0.009
	2	-0.10	-0.15	0.00		
	2	0.23	0.33	0.01		
	3	0.27	0.38	0.01	0.009	0.003
	3	0.14	0.19	0.01		
	3	0.17	0.24	0.01		
	4	0.75	1.07	0.04	0.037	0.007
	4	0.66	0.94	0.03		
	4	0.93	1.34	0.04		
OS2	1	-0.25	-0.36	-0.01	0.007	0.016
	1	0.35	0.51	0.02		
	1	0.32	0.46	0.02		
	2	0.09	0.13	0.00	0.007	0.004
	2	0.10	0.15	0.00		
	2	0.26	0.37	0.01		
	3	0.24	0.34	0.01	0.012	0.003
	3	0.34	0.48	0.02		
	3	0.21	0.31	0.01		
	4	0.23	0.32	0.01	0.009	0.002
	4	0.18	0.26	0.01		
	4	0.14	0.21	0.01		
LLDPE	1	0.35	0.51	0.02	0.014	0.002
	1	0.26	0.37	0.01		
	1	0.27	0.39	0.01		
	2	0.18	0.26	0.01	0.010	0.002
	2	0.24	0.35	0.01		
	2	0.19	0.27	0.01		
	3	0.15	0.22	0.01	0.010	0.002
	3	0.25	0.36	0.01		
	3	0.20	0.29	0.01		
	4	0.18	0.26	0.01	0.010	0.002
	4	0.17	0.24	0.01		
	4	0.25	0.36	0.01		

Table 60. Migration of NaCl into 3 % acetic acid as calculated from observed migration of sodium (Na), respectively

	Sample #	Abs	Na μg/30ml	NaCl μg/30ml	NaCl mg/L	Ave	Std
Tube(OS2)	1	0.8070	1.1145	2.83	0.09	0.129	0.032
	1	1.1121	1.8757	4.77	0.16		
	1	0.9874	1.5646	3.98	0.13		
	2	1.0253	1.6592	4.22	0.14	0.139	0.004
	2	0.9943	1.5818	4.02	0.13		
	2	1.0324	1.6769	4.26	0.14		
	3	0.8804	1.2977	3.30	0.11	0.107	0.003
	3	0.8616	1.2507	3.18	0.11		
	3	0.8554	1.2353	3.14	0.10		
	4	1.0221	1.6512	4.20	0.14	0.186	0.040
	4	1.3499	2.4691	6.27	0.21		
	4	1.3552	2.4823	6.31	0.21		

Table 61. Migration of $CaCl_2$ into 3 % acetic acid as calculated from observed migration of calcium (Ca), respectively

	Sample #	Abs	Ca μg/30ml	$CaCl_2$ μg/30ml	$CaCl_2$ mg/L	Ave	Std
Tube(OS2)	1	0.2049	1.7410	4.83	0.16	0.160	0.001
	1	0.2026	1.7204	4.77	0.16		
	1	0.2025	1.7195	4.77	0.16		
	2	0.2794	2.4087	6.68	0.22	0.226	0.003
	2	0.2841	2.4507	6.80	0.23		
	2	0.2852	2.4606	6.83	0.23		
	3	0.2834	2.4445	6.78	0.23	0.199	0.049
	3	0.2861	2.4686	6.85	0.23		
	3	0.1825	1.5404	4.27	0.14		
	4	0.2364	2.0233	5.61	0.19	0.188	0.001
	4	0.2394	2.0502	5.69	0.19		
	4	0.2365	2.0242	5.62	0.19		

Table 62. Migration of Fe_2O_3 into 3 % acetic acid as calculated from observed migration of iron (Fe), respectively

	Sample #	Abs	Fe μg/30ml	Fe_2O_3 μg/30ml	Fe_2O_3 mg/L	Ave	Std
Tube(OS2)	1	0.1482	1.3361	1.91	0.06	0.064	0.000
	1	0.1497	1.3500	1.93	0.06		
	1	0.1493	1.3463	1.92	0.06		
	2	0.1293	1.1606	1.66	0.06	0.056	0.000
	2	0.1313	1.1792	1.69	0.06		
	2	0.1302	1.1690	1.67	0.06		
	3	0.1924	1.7465	2.50	0.08	0.084	0.001
	3	0.1933	1.7549	2.51	0.08		
	3	0.1952	1.7725	2.53	0.08		
	4	0.1438	1.2953	1.85	0.06	0.061	0.001
	4	0.1424	1.2823	1.83	0.06		
	4	0.1411	1.2702	1.82	0.06		