1995

The Permeation of volatile compounds through acrylonitrile polymers films

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THE PERMEATION OF VOLATILE COMPOUNDS THROUGH ACRYLONITRILE POLYMERS FILMS

By

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A Thesis

submitted to the
Department of Packaging Science
College of Applied Science and Technology
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Rochester Institute of Technology

1995

College of Applied Science and Technology
Rochester Institute of Technology
Rochester, New York

CERTIFICATE OF APPROVAL

M.S. DEGREE THESIS

The M.S. degree thesis of Juan Ramiro Escobar
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by the thesis committee as satisfactory
for the thesis requirements for the
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Date February 17, 1995

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ACKNOWLEDGEMENTS

This thesis is dedicated to my wife, Claudia. She has been my inspiration and my support. Without her loving dedication and confidence it would never have been completed.

I wish to acknowledge MAS Technologies for providing their equipment and technical assistance. Special recognition is made of Joseph McCaul from British Petroleum for providing the Barex^{R} material and his knowledge about it; and of Mobil Corporation for providing their films.

Additional thanks to the faculty of the Department of Packaging Science at R.I.T. for their guidance and support. They made easier the experience of learning.

ABSTRACT

The increasing use of polymeric films for packaging food is challenging the industry with two very critical facts: aromatic constituents of foodstuffs can either be absorbed by the packaging materials or permeate through the polymers and escape from the package.

The packaging and food industries are constantly researching new packaging materials and systems which present alternatives to overcome these problems. In order to evaluate polymers' performance, it is then necessary to develop new testing equipment to prove their barrier efficiency.

This study analyzed and compared the characteristics of three barrier materials: Barex[R] 210, Bicor[R] 84, and Bicor[R] 70 by means of one testing system, which has been recently developed, offering to the industry a useful tool to evaluate the barrier characteristics of the packaging materials. The system uses an isostatic test method and incorporates a flame ionization detector (FID), precise temperature and flow rate control, which allowed to determine the permeability rate, the diffusion rate, and the solubility values of pyridine, and to correlate them with the values obtained from the volatile compounds of fresh ground coffee.

The outcome of the experiment proved that all three films tested are very good barrier materials. Nevertheless, it is necessary to continuing experimenting on the same materials with the same equipment, using different procedures, to find significant figures that could lead to conclusive results about which material has the best barrier characteristics.

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Chapter 1

INTRODUCTION

SHELF LIFE EXTENSION

Since the beginning of last century, when Nicholas Appert first canned food, food packaging has evolved to meet the requirements of the industry and the demands of the consumer. However, the methods and materials used to package food have changed more in the last 15 years than over the preceding 150 years. The impact of those changes and the concern with the quality, safety, shelf life and nutritional content of packaged foods have led to an increasing interest in the interactions between food products and food packaging materials.[1]

From the moment of harvest foods begin to change and degrade from their original composition. Biochemical, chemical, and physical activities all contribute to change in characteristics of foods. Although some of those changes may be desirable, as in the case of aging of cheeses and wine, development of yogurt, some other changes, such as gradual loss of color, texture, flavor, aroma and nutrients, are

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[1]Joseph H. Hotchkiss, Preface to Food and Package Interactions. American Chemical Society, ASC Symposium Series 365 at the 193rd meeting. (Denver, CO.: April 1987), xi.

not.[2] These changes occur in food mainly because of microbiological decay: lipid, flavor, and nutrients oxidation; moisture loss or gain; flavor and aroma scalping by the packaging materials; and migration of packaging components to the food products.[3]

The food packaging and the food industry utilize all the principles of packaging. Those principles are to preserve, protect, distribute, and merchandise the products. Hence, packaging is responsible for the shelf life of the product. Shelf life is defined as the ability to maintain the original quality of the product until it is fully consumed by the user.

Packaging is only one factor at work in the preservation of food. The purpose of packaging food is to isolate food from contact with elements and/or microorganisms which spoil it, and the mechanisms that interact between product and packaging have to be fully understood in order to achieve the goal of a prolonged shelf life which is well beyond the specified period of use of the products. The distribution system has lengthened the required shelf life and has compelled the product and its packaging to become one integrated unit. The characteristics of one determines

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[2]Stanley Sacharow and Roger C. Griffin, Principles of Food Packaging. (Westport, CT.: 1980) p. 73

[3]William Brown, Plastics in Food Packaging, Properties, Design, and Fabrication (New York : Marcel Dekker Inc., 1992) p. 360

the characteristics of the other.[4] This is the reason why packaging must offer the food industry all the tools that will allow it to move products from the place where they are produced to distant locations where they will be used.

Plastics in Food Packaging

One of the main contributions of packaging to the food industry has been plastics. In the last few years, the development of high barrier polymer (HBP) films has been of critical importance to the improvement of the food packaging industry. Even though glass and metal containers are practically the only impermeable packaging barriers, more and more food items are being considered for packaging in flexible pack-ages due to cost reductions in materials and distribution systems, lighter weight, more resistance to breakage and shattering, and lower energy use in order to fabricate the packages. Unlike metal containers, plastic packaging can also be transparent and does not change the taste of the product when in direct contact. Finally, plastic packaging is flexible, can be reheated with microwave, and enjoys general consumer preference.[5]

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[4] J. K. Cage, "Introduction to Food Packaging," in Food Packaging Technology, ASTM STP 1113, ed., Debra Henyon, (Philadelphia, PA.: ASTM, 1991) p. 3

[5] John D. Culter, "Improving barrier through orientation in processing," in Plastic Film Technology. ed. Kier M. Finlayson. (Lancaster, PA.: Technomic Publishing Co.,1989) p. 51

Despite these advantages of HBP films, there is no universal flavor-aroma barrier among them.[6] Therefore, plastics have to be designed to suit the different requirements of different products. The industry and the market are evolving entities that are constantly challenging the packaging field. For instance, the adoption of new technologies in food packaging, such as modified atmosphere and gas flushing, requires a better understanding of the interaction between foodstuffs and packaging materials in order to overcome mass transfer problems from and towards the products.[7]

Flavor and Aroma

Flavors and aromas are important elements of food because people want food which tastes good, retains its original flavor, and is free of alien odors.[8] Flavors and aromas are chemical and physical stimuli to which people respond. They include an extensive array of chemical compounds whose presence determine both the original quality of foodstuffs and the ability to retain that quality during the shelf life. Flavor and aromas in food can be affected by oxidation, hydrolysis, decomposition or loss of the compo-

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[6]Brown, Plastics in Food Packaging. p. 323

[7]Ibid., p. 293

[8]P.T. DeLassus and G. Strandburg, "Flavor and Aroma Permeability in Plastics," in Food Packaging Technology, ed., Debra Henyon. pp. 64-73

nents, either by being absorbed by the packaging materials, or by penetration through the packaging materials.[9]

Polymers can absorb the components of flavor and aroma of food products, either across all the food components, or selectively. The former will lead to flavor diminution and the latter to imbalance while retaining intensity of some of the residual compounds. This is a critical factor because a weak good flavor is more acceptable than a strong off-flavor.

Coffee Packaging

A strong pleasant food aroma which is positively perceived by consumer very often has a high concentration of volatile components. Coffee is an example of a product with a highly volatile aroma content. It owes its distinctive flavor and aroma to 655 compounds which have been identified in roasted coffee aroma. These compounds belong to 18 different chemical families. The compounds with more influence on the aroma of the beverage, are not necessarily the most abundant in the ground coffee aroma.[10] However, the slightest loss of any of those components will affect the quality that the consumers expect in the product.

To most coffee drinkers, the smell of a newly-opened

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[9]Brown, Plastics in Food Packaging. p. 90

[10]Ivon Flament, "Coffee, Cocoa, and Tea." In Volatile Compounds in Food and Beverages. ed. Henk Maars. p. 618.

container of coffee is pure perfume and is certainly the principal reason why coffee has such wide acceptability throughout the world.[11] Coffee, like wine, is classified according to its fragrance, aroma, taste, nose, after taste, and body. However, because of its highly volatile nature, the aroma does not last very long unless protection is provided.

Coffee, when packed under normal atmosphere conditions, can lose taste and odor and turn stale in less than a week. When coffee ages, its aroma degrades from flat to old to sharply rancid. As coffee ages there is a loss in flavor and an increase in unpleasant taste when brewed. Hence, one of the ways that shelf life of coffee can be substantially extended is to pack it under modified atmosphere conditions.[12] In Japan and Europe, coffee is packaged in plastic, but in the United States it is packaged mainly in glass and metal containers. These are the most effective barrier materials, but they are difficult to use under modified atmosphere conditions. This is probably one of the key reasons why packing for coffee is moving to flexibles.

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[11]Henry B. Heat, Source Book of Flavors. (Westport, CT.: The AVI Publishing Co, 1981). p. 164.

[12]Michael Sivetz, Coffee Processing Technology (Westport, CT.: The AVI Publishing Co., 1963) Vol. 1, p. 519

THE PURPOSE OF THE THESIS

The results of scientific studies done on high barrier polymers in the last two decades show their high potential within the packaging industry. The main goal of this thesis is to know the procedures of some of these experiments, to use them performing physical tests on some barrier materials, using coffee as product case, to gather data, to evaluate the results and to present them as reference for packaging professionals.

SIGNIFICANCE OF THE STUDY

Several studies have been done on both the volatiles present on coffee aroma and the phenomena of gas transmission through barrier polymers. It is important to point out that the researchers look either for the way a particular class of compounds interacts with different polymers or for the transport characteristics of gases and the relation between several given compounds and a given material, to understand the change of a specific product.[13] In the case of coffee, it is of particular interest to note the amount of studies using different techniques to determine the number and type of volatile compounds present in its fragrance, as well as the relative significance of each

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[13]Sara J. Risch and Joseph H. Hitchkiss, Preface to Food and Packaging Interactions. American Chemical Society, ASC Symposium Series 473 200th meeting (Washington, D.C.: August 1990), xiv.

individual component on the overall nature of the aroma.[14]

Although procedures used here are similar to the ones used in these earlier studies, this investigation differs in some points:

1. The goal is to determine the transmission behavior of only one volatile, pyridine, which is present in coffee aroma, to determine what its interaction is with the flexible barrier materials and then follow the same volatile and its behavior when using freshly ground coffee.

2. One high-barrier polymer which has been found to be useful in packaging aromatic foodstuffs is Barex[R], an acrylonitrile methylacrilate copolymer. To test the high barrier properties of Barex[R], two flexible structures which are commercially available have been selected. They are used in the experiment as controls.

3. There have been few studies about the interaction of coffee and flexible materials. This will consider the interaction of coffee and materials tested.

The price of coffee in the American market is dependent on several external elements. Research in packaging materials could result in decreasing this dependence and prevent losses in the $ 3.3 billion American coffee

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[14]Terrence A. Lee, Rebecca Kempthorne, and James K. Hardy. "Compositional Changes in Brewed Coffee as a Function of Brewing Time." Journal of Food Science. 57, No.6, (1992) pp. 1417-1419

market[15] which is being challenged by many different factors. For example, in 1994 there was an increase of 45% in the coffee price[16] due to recent events in three of the major coffee producing countries: massacres in Rwanda, frosts in Brazil, and pests in the crops in Colombia. The more quality aware coffee consumer of today is also demanding a better and more diverse product. Per capita consumption of regular coffee has decreased from 3.2 cups per day in the 60's to 1.8 cups in 1992.[17] However, there has been an increase of the consumption of specialty and gourmet coffees at a steady 9.3% average annual rate, making this a $1.1 billion industry with demands for more efficient packaging materials.[18] Therefore, coffee roasters are changing from the traditional glass and metal containers, which still account for 80% of the market, to the more convenient and economical high barrier polymer films.[19]

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[15]John C. Maxwell Jr., "specialty Coffee Sales Perking in Flat Markets," Advertising Age. 64 (June 14 1993) p. 46.

[16]Dori Jones Yang, "Trouble Brewing at the Coffee Bar." Business Week. (August 1 1994) p. 62.

[17]Carrie Goerne, " Coffee Consumption Down but Sales of Exotic Blends Perk up," Marketing News. 26 (July 20 1992) p. 22.

[18]Peg Masterson, " Top 100 Succumbs to Specialty Coffee Aromas," Advertising Age. 64 (sept. 29 1993) pp. 30-34.

[19]Dietmar Reinke, "Flexible Packaging of Ground Roasted Coffee," in Plastic Film Technology. ed. Kier M. Finlayson. pp.70-79.

STATEMENT OF THE PROBLEM

THERE IS A DEMONSTRATED NEED TO STUDY THE INTERACTION OF FLAVOR AND AROMA AND PLASTIC PACKAGING TO RETAIN THE QUALITY OF FOOD PRODUCTS

Because of the tendency in the food industry to move away from glass and metal containers to more inexpensive and convenient plastic packages, it is necessary to give special attention to the interaction of flavor and aromas between plastics and food. Flavor compounds are often volatile and they must be retained by barriers in packages in order to preserve the quality of the products.

THE FIRST SUBPROBLEM

THE STUDY OF THE PHENOMENA OF PERMEABILITY, DIFFUSION, AND SOLUBILITY IS NEEDED TO EXPLAIN CLEARLY WHY FLAVOR AND AROMA LEAK THROUGH TIGHTLY-SEALED PLASTIC PACKAGES

Flavors and aromas exhibit similar behaviors to gases and liquids in permeating plastic membranes. However, they are more likely to interact strongly with plastics because their compounds tend to have lower molecular weight. Thus, they can permeate more easily through plastic films or be absorbed by scalping (solution) into the polymers from which the packages are made. Their coefficients are more strongly affected by concentration or pressure, and their losses from foods to package components occur by solution, governed in rate by the magnitude of the diffusion coefficient, followed by penetration, if enough time elapses.[20] The compounds dissolve and diffuse in plastics in varying degrees. Some do it rapidly, and thus they are scalped from the food.[21]

It makes no difference whether flavors or aromas are lost by absorption into the package components or by permeation (P); any migration from the food is considered a loss. Capacity for sorption is determined by the solubility coefficient (S), whereas the speed of sorption is fixed by the diffusion coefficient (D). Knowing the numerical values of D and S, one may calculate how much of a volatile compound will be taken up and how much transmitted after any elapsed time. It is very important to know the solubility values of essential flavor ingredients in certain polymers, in order to avoid flavor scalping. For purposes of this study, scalping will be defined as the loss of flavor or aroma constituents by absorption into the film, i.e., the solubility coefficient. Since the flavor compounds are normally present in low concentrations in foodstuffs, there is a potential risk to lose the aromatic constituents due to absorption by the package film. The important concerns in

[20]Brown, Plastics in Food Packaging. p. 323

[21]Ibid., p. 300

flavor and aroma migration then are:

a. What is the capacity of the package material for solution?

b. How fast does solution occur?

c. What is the magnitude of penetration during the expected shelf life?[22]

THE SECOND SUBPROBLEM

THE MARKET OFFER OF HIGH BARRIER MATERIALS IS VERY LIMITED. THE SEARCH FOR OTHER POTENTIAL MATERIALS MAY BE EXPENSIVE AND USELESS BECAUSE MATERIALS CURRENTLY AVAILABLE ARE ENOUGH TO SUPPLY THE NEEDS OF THE INDUSTRY.

Packaging engineers are in constant search for new and more convenient materials which could become alternatives to current, traditional packages. Until the early 1970's only metal, glass and polyvinyldene chloride films (PVdC) would provide high barrier protection for the food products industry. In 1973, ethylene vinylacetate (EVAL), and ethylene vinyl alcohol (EVOH) resins were commercialized by Kuraray Co. Ltd. in Japan. Multilayer packaging structures containing EVOH resins quickly demonstrated their ability to provide high barrier protection for a variety of products. By the mid 70's, EVOH resins had been introduced to the American market: companies such as American Can and Cryovac began producing HBP flexible films for the packaging of meat

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[22]Brown, Plastics in Food Packaging. p. 301

and cheese products.[23] Acrylonitrile copolymers, which had been banned from the soft drink industry, offer interesting possibilities as packaging material to the coffee industry because their ability to retain flavors and aromas.

Acrylic multipolymers produced using acrylonitrile (AN) as a comonomer with methyl methacrylate (MMA) and rubber modifier to produce a tough and transparent resin, are used mainly in health care and food packaging. Their gas and chemical barrier properties can be raised by increasing the nitrile content above 25 percent. These of high-nitrile resins (HNR) were produced during the 60s and 70s to supply the beverage industry with new types of bottling resins. Unfortunately, because of the potential migration of acrylonitrile from the bottle to the beverage, they were banned by the Food and Drug Administration. However, they were allowed to be used with non-beverage food applications at temperatures lower than 150^0F.

Some of the barrier properties that make high nitrile resins interesting for this study are:

Oxygen Barrier Properties

High nitrile resins have the greatest barrier properties to oxygen of any plastic material used for single layer containers. 0.8 cm^3*mil/100 in^2 at 24 hrs-atm. They are only

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[23]Eric B. Schaper, "High Barrier Plastics Packaging and EVOH Resins," in Food Packaging Technology. ed. Debra Henyon. pp. 31-33.

surpassed by EVOH and PVdC, which are used as components of multilayer structures.

Scalping

High-nitrile resins are known as the best anti-scalping plastic materials. They do not absorb aromas or flavors from the product. Therefore, the product does not become flat or weak.

Chemical Resistance

High nitrile resins (HNR) offer the highest chemical resistance among monolayers. HNR containers can be affected at temperatures above 73^0F by methylene chloride, trichloroethylene, ethyl acetate, acetic acid and some ketones, esters and solvents. They are compatible with naphtha, turpentine, shellac, cooking oils, moderately strong acids, and perfumed products.

Because of its unique combination of barrier properties, HNR resins ensure product freshness, extended shelf life and retention of natural aromas and flavors. The inclusion of an acrylate makes the polymer an excellent gas barrier, but reduces its heat resistance.

THIRD SUBPROBLEM

THE AMOUNT OF VOLATILE COMPOUNDS MAKES COFFEE ONE OF THE MOST DELICATE PRODUCTS. IT REQUIRES HIGH EFFICIENCY IN BOTH ITS PACKAGING AND IN ITS ABILITY TO MAINTAIN INTEGRITY ON THE SHELF FOR A CONSIDERABLE PERIOD OF TIME

Coffee aroma is a complex mix of more than 650 compounds, in which the presence of pyridine has been identified in both green and roasted coffee. After it has been roasted, coffee is very susceptible to undesirable changes and may easily pick up foreign flavors and odors. Ground coffee loses flavor twice as fast as roasted whole beans. It also quickly loses its intrinsic physical and chemical properties, as well as the aromatic and flavor constituents which make coffee fresh and fragrant while brewing.

Coffee can also be upset by oxygen and moisture absorption, which are the main factors affecting the shelf life of the product. Therefore, in order to keep the attributes of roasted coffee, storing conditions and the packaging are of critical importance. In addition, the release of CO_2 and other volatiles occurs during storage, which is especially significant during the roasting process and the 24 hours after beans have been roasted and ground. This loss of volatile compounds highly influences the taste of the beverage. Although the absorption of oxygen and moisture by ground coffee and the release of CO_2 and aromas can be simultaneous, there is no known relationship between both activities. Moisture is far more degrading than O_2.[24]

SCOPE AND OBJECTIVES OF THE STUDY

This study has two main objectives:

1) To determine if a monolayer film of acrylonitrile methylacrilate copolymer maintains or improves the flavor and aroma barrier performance compared to other thermoplastic resins. These resins are used as components of multilayer structures which are currently available in the market as high barrier packaging.

2) To test the scalping charateristics of all the materials undergoing the experiment.

The method utilized was based on the isostatic gas chromatographic procedures already used in several studies. In this research, a method able to detect aromatic molecules and to quantify the barrier properties of the different polymers submitted to the experiment was used. In order to prove that the model used and the conclusions reached are accurate, pyridine, one of the elements present in the coffee aroma was used as permeant. The pyridine was used 99.9% pure to calibrate the system, and freshly ground coffee used as case study. A linear regression model will then be necessary to determine the barrier properties of the films.

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[24]Sivetz, Coffee Processing Technology. p. 519.

The equipment that was used was the MAS 2000, which is being developed by MAS Technologies. The MAS 2000 is an organic permeation detector which includes a gas chromatograph, a very sensitive flame ionization detector, and an analytical computer program. This system detects organic volatiles in the range of a few parts per billion (ppb), processes the information obtained, makes the statistical analysis, and renders highly accurate results in just minutes instead of days.

LIMITATIONS

For the purpose of this paper, the study was limited to researching the permeation characteristics of pyridine through acrylonitrile methyl acrylate copolymer films. To avoid bias in the results, a monolayer film, neither coated nor laminated to any other polymer was used. Also, to simplify the experiment, taste was not considered.

This study covered the aroma barriers of the materials used for the experiment. Other barrier characteristics, such as moisture, oxygen, and UV light were not researched. Thus, more research will be needed to draw any conclusion about whether or not acrylonitrile methyl acrylate films will perform well as universal barrier packaging materials.

DEFINITIONS AND TERMS

Absorption

Absorption is the penetration in bulk of one material throughout a second material. It is usually associated with the formation of strong chemical bonds an is rarely reversible at ambient temperatures. Dissolution of gases in liquids frequently involves absorption forces. The difference between absorption and adsorption is that the former involves fairly uniform penetration of the absorbent matrix, while the latter occurs predominantly in the surface layers, and the forces involved in adsorption are very much less than chemical forces of the absorption process.

Adsorption

Adsorption is a process which occurs at the surface of a liquid or solid as a result of attractive forces between the adsorbent and the solute. The forces could be physical, such as Van der Waals forces or chemical as in the case of hydrogen bonding. Physical adsorption is involved with lower heat while chemical adsorption involves higher energy changes. As a result, chemical adsorption is stronger than physical adsorption.

Diffusion

Diffusion is the process by which molecules or similar particles move spontaneously from a region where they are present at relatively high concentration into regions of lower concentration. At ordinary temperatures molecules are in constant random motion; hence the number of molecules moving out of a given volume of high concentration will be greater than that moving into it, and this process will continue until the concentration is uniform throughout.

The diffusion rate is influenced by different factors such as concentration, temperature, molecular weight, electrical and magnetic forces. The rate of diffusion is governed by the concentration gradient because the greater the difference of concentration in both areas, the more rapidly the molecules diffuse from the higher concentrated area to the lower one. Diffusion rate is also directly related to temperature. Any increase in temperature will increase diffusion because it makes the molecules move faster. In gases, molecular weight is inversely proportional to diffusion because lighter molecules travel faster than heavy ones.[25]

Food Spoilage

Food spoilage is any change in foodstuffs that makes

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[25] Academic American Encyclopedia. 1994 ed. s.v. "Diffusion." by George Gorin,

the product unacceptable for the consumer.

High Barrier Polymers (HBP)

High barrier polymers are considered those which have a high resistance to gas transmission and also those materials which impede the transfer of a substance into or out of a food product. i.e., PVdC, EVOH, and nitriles and multi-layer structures made of combinations of those materials.

Migration

Migration is the mass transfer of molecules between plastics and food. It can operate in two ways, i.e., from plastic to food, which is the more normal meaning, or from food to plastic, which is better known as scalping. Polymeric materials may contribute to food spoilage by giving away aromas from such things as residual mononomers, solvents or processing additives. [26]

Permeation

Permeation is the transport of a penetrant through a homogeneous membrane. It is usually considered to occur by the following process: solution (condensation and mixing) of the gas or vapor in the surface layers, migration to the opposite surface under a concentration gradient, and evapo-

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[26]John H. Briston, Plastic Films. 3th ed. (Essex, UK.: Longman Scientific & Technical, 1988) p. 144.

ration from that surface into the ambient phase.[27]

Scalping

Scalping is the solution of fugitive molecules into packaging materials in contact with the food product. Its main direct consequence to food is on organoleptic properties, but it can have an effect on the nutritional quality of food if certain components are lost to a significant extent.[28]

Shelf Life

Shelf life is defined as the period between the manufacture and the use of a food product, during which time the product must maintain a state of satisfactory quality in terms of nutritional value, taste, texture, and appearance.

Solution

Also defined as scalping. Solution is the amount of any substance taking up residence in the barrier or that will dissolve in a given amount of another substance and is typically expressed as the number of parts by weight dissolved by 100 parts of solvents at specific temperature

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[27]C.E. Rogers, "Permeation of Gases and Vapors in Polymers'" in Polymer Permeability. ed. J. Comyn. (Essex, UK.: Elsevier science Publishing Co., 1986) pp. 11-73.

[28]Briston, Plastic Films. p. 144.

and pressure or as percentage by weight or by volume.[29]

Solubility Coefficient

The solubility coefficient is a thermodynamic term that describes how many permeant molecules move in a polymer host. It is determined by all the usual parameters of solution including temperature, chemical activities, and intermolecular interactions plus the state of the polymer relative to its glass transition temperature.[30]

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[29]Brown, Plastics in Food Packaging. p. 131.

[30]P.T. DeLasssus and Gary Strandburg, in Food Packaging Technology. Ed. Debra Henyon. p. 65.

Chapter 2

REVIEW OF RELATED LITERATURE

FOOD SPOILAGE

Spoilage is the result of change that makes food unacceptable for the consumer. Spoilage is a major cause of food loss. Much of the food fails to reach the consumer. Food become unpalatable or unsafe to eat after it has been purchased; thus, spoilage is a problem for both the food industry and the consumer. The huge amount of research done on food processing and preservation have helped to solve some problems and allowed at least the developed countries to have the greatest and safest supply of food ever. Nevertheless, the development of new varieties of foods and food processing technologies will continue to make food spoilage an ever-present problem.[1]

There are two type of food degradation: loss of nutritional quality and sensory characteristics, such as color, odor, and flavor, and non-detectable characteristics due to the presence of harmful bacteria. Foodstuffs can be degraded by extrinsic sources or by intrinsic sources. In

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[1]Brackey, "Food Degradation," In Encyclopedia of Food Technology.

many foods however, more than one cause contributes to the spoilage of the product. It is possible to classify the causes affecting food as follows:

* Microbial growth
* Biochemical or physiological deterioration
    - Oxygen reactions
    - Water and moisture activity
    - Aroma and flavor gain and loss
* Physical damage

Packaging is responsible for acting as a barrier and maintaining the proper conditions to preserve the quality of foodstuffs. However, it is just part of a whole complex system which has to be considered along with other disciplines, necessary to assure adequate the shelf life of products.

Microbial Growth

Microorganism growth is the main cause of food spoilage. Bacteria, mold and yeast are the type of microorganisms that commonly affect food. The Environmental conditions which favor microorganism growth, and the kind of damage that they provoke to food, depend on the type of pathogenic agent. The following conditions need to be kept under control in order to prevent decomposition of foodstuffs by microorganisms:

Temperature: Most microorganisms are mesophyles, growing at a temperature range of 10°C to 50°C.

Acid/Alkaline PH: Different microorganisms require a specific Ph range, which beyond its lower or higher limits growth is inhibited. The ideal environment for bacteria is neutral (Ph of 6.0 to 7.5); molds and yeasts prefer acid environments (Ph of 3.5 to 5.5)

Oxygen: The presence of anaerobic, aerobic, and facultative microorganisms has to be prevented. Therefore, the oxygen level has to be controlled depending on the potential attack of any specific microorganism.

Water Activity: Most bacteria favor a high water content with water activity of 0.94, while most yeast grow above 0.87 and molds tolerate content of 0.75 or 0.70. However, the water activity of the foods is more critical than the water content of the product, because it foments not only the microorganism reactions but also the chemical and bio-chemical activities occurring in the foods rather than on the water content itself.[2]

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[2]Toshimasa Yano, "Physical Properties and Microbiology of Foods" in Food Packaging. Takashi Kadoya, ed., (San Diego, CA.: Academic Press, Inc., 1990) pp. 17-22

BIOCHEMICAL DETERIORATION

Because foods are composites of various naturally occurring chemical mixtures, foods are subject to chemical reactions and biochemical processes, many of which lead to deterioration of quality.[3]

Oxygen Reactions

The presence of oxygen can cause changes in foods that are often perceived as spoilage. Many of this changes are catalyzed by oxidative enzymes, but others are caused simply by the reaction of oxygen with food components. The red color of fresh meats turns brown by the reaction of myoglobin with oxygen. Lipids also react with oxygen and develop a rancid flavor in foodstuffs. Limiting exposure of foods to oxygen prolongs shelf life of products and assures the highest quality and nutrient retention for most foods.[4]

It is not possible, however, to eliminate oxygen completely from food, nor from inside the package. Also in permeable packages, it is impossible to prevent oxygen intrusion, so the key point is to maintain O_2 at a concentration lower than the damaging level.[5]

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[3]Bracket,"Food Degradation" in Encyclopedia of Food Technology.

[4]Ibid., "Food Degradation."

[5]Brown, Plastics in Food Packaging. p. 13

Moisture Gain and Loss

Water is present in all foods. Retention or removal of water under controlled conditions is vital to minimize biochemical and chemical changes that lead to spoilage of foods, development of off-flavors, and variation of texture, color and aroma. Upper and lower limits of moisture are also critical to the preservation of certain foods, necessary for the retention of original quality in all foods, and also in the control of microorganisms which may relate in some instances to human safety in food consumption.[6]

Water Activity (a_w), the measure of the tenacity of any substance to retain water, expresses the relationship of relative humidity of the environment with the content of water in the food. The Water Vapor Transmission Rate (WVTR) is the rate of moisture transmission through the material structure. a_w and WVTR must be determined to control the packaging barrier in order to prevent excessive dryness or moisture in the product.

Knowing the initial and tolerable moisture range (minimum and maximum), and the environmental conditions of temperature and humidity, the moisture content of the food can be calculated for any package material of known transmission and geometry, and for all lengths of exposure time.[7]

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[6]Brown, Plastics in Food Packaging. p. 89

[7]Ibid., p. 89

Flavor and Aroma Gain and Loss

Of the five senses of taste, smell, sight, touch, and hearing, the two which most concern food preservation and packaging technology are taste and smell. A survey undertaken at the University of Delaware Department of Food Science, initiated in 1990 and completed in 1991, rated flavor and aroma preservation by food packages as extremely important by 94.7% of the population.[8]

Important in certain flavorful foods and beverages is the retention of flavor and aroma substances and the rejection of invading elements which could adversely affect food quality.[9] Flavor and aroma compounds are usually highly volatile, and typically are very dilute gases. Their presence in the foodstuffs, which is easily detectable by smell, are normally in the atmosphere only at sub ppm levels. Therefore, they can be easily lost to the environment due to diffusion.

Additionally, the degree of tainting which can occur to food products is not only dependent on the atmospheric concentration of organic volatiles but also on the permeability of the packaging material. In some European countries, it is now a legal requirement that packaging materials containing

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[8]W. Guise, "Organoleptics and Packaging Materials," Packaging. (August 1991) pp. 4-8.

[9]Charles A. Harper. Handbook of Plastics, Elastomers, and Composites. 2nd. ed. (New York : MacGraw-Hill Inc., 1992) p. 42.

foods should be capable of retaining the flavor of those foods and prevent the tainting of the foods by the permeation of odorous vapors.[10]

PHYSICAL DAMAGE

Physical damage usually has immediate and obvious consequences. However, damage can also have more subtle or delayed effects on the food. Punctures and abrasions damage skins and peels, and allow the access of microorganisms. Other physical damages such as odor adsorption, specially food high on lipids content, are only obvious weeks later. Consequently, packaging or other barriers to migration of odors or flavors must often be used to protect such products.[11]

Types of Physical Damage

Mechanical: Inert objects strike, abrade or puncture the food.

Freezing Damage: Ice crystals freeze within tissues and break the cells of the product.

Living Creatures: Insects, small rodents, and even large animals feed upon the food, and some actually live in the food.

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[10]Guise. Packaging pp. 4-8.

[11]Bracket, "Food Degradation." In Encyclopedia of Food Technology.

THE COFFEE INDUSTRY AND PACKAGING

WHAT IS COFFEE

The word coffee is derived from the Arabic *Qahwah*. It was first known by people in the Arabic world and introduced to Europe through Turkey. Drunk as stimulant beverage today, it was first used as food, then fermented and used as wine and medicine. In the 13th century, coffee was roasted to prepare a beverage similar to the one we know today.

Coffee berries are obtained from a small evergreen shrub that grows in the highlands of the tropics, at 2000 to 6000 feet above sea level and a temperature around 70^{0}F. Once these are ripened on the shrub, they are picked by hand, taken to processing facilities and passed through a mill where their red skins are peeled off. Once released from their skins, the berries split into two beans. These are then washed and dried, yielding the green coffee beans ready for commerce. In this state, this commodity becomes one of the most important articles of international trade.[12]

The composition of green coffee beans can remain basically the same for about 3 years, if they are stored at low relative humidity and away from contaminating odors. In this stage, coffee is not yet ready for brewing because it is bitter and has an unpleasant smell. The characteristic

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[12]Heat, Source Book of Flavors. pp. 164-166

aroma and flavor of coffee is obtained only after roasting.[13]

Coffee Characteristics/Stability

After it has been roasted, coffee is very susceptible to undesirable changes, and may easily pick up foreign flavors and odors. Ground coffee loses flavor twice as fast as the roasted whole beans. It also quickly loses its intrinsic physical and chemical properties, and the aromatic and flavor constituents which make coffee fresh and fragrant when is being brewed.

The quality of coffee can also be spoiled by oxygen and moisture absorption which are the main factors affecting shelf life of the product. Therefore, in order to keep the attributes of roasted coffee, storage conditions and packaging are of critical importance. Another factor to be considered during storage is the release of carbon dioxide (CO_2) and volatile aromas, specially when roasting. A significant part is also lost during the 24 hours after the beans have been ground, and then CO_2 is lost more slowly.[14] Permeability of the package to CO_2 release from roasted coffee may be critical in flexible coffee packages, especially when coffee has been packaged immediately after roasting and grinding. It is necessary for a certain amount

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[13]Heat, Source Book of Flavors. pp. 164-166.

[14]Sivetz. Coffee Food Technology. p. 519.

of CO_2 to be released in order to prevent ballooning and possible rupture of the walls.[15]

Although the absorption of oxygen and moisture and the release of CO_2 and aromas can be simultaneous, there is no known relation between both activities. Moisture is far more detrimental than CO_2.[16]

Heiss showed in an experiment in 1960 how fast unpacked, roasted coffee degrades in the presence of moisture. His work also clearly illustrates the importance of high barrier polymers in packaging for coffee. When the moisture content of roasted coffee is raised in about 1% (from 1.4% to 2.6%), a stale odor is detected in 14 to 20 days.[17]

The relation that Heiss found between moisture and coffee degradation is as follows :

RH	Time to develop stale taste
0%	3-4 weeks
50%	7-8 days
100%	3-4 days

Coffee Degradation by Flavor and Aroma Loss

Composition of Flavor and Aroma: The composition of food flavors and aromas is usually a very intricate blend of sometimes hundreds of several organic volatile and non-

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[15]Sivetz, Coffee Food Technology. p. 521.

[16]Ibid., p. 519.

[17]Ibid., p. 520.

volatile elements. The concentration level and the presence of them in foodstuffs determine the grade of acceptance of the product. The aroma of roasted coffee is the key factor influencing the consumers. Once roasted, coffee aroma turns into a very complex blend of flavor sensations. Coffee aroma is the resulting product not only of the caramelization of sugars, but also of the following:

* simultaneous hydrolysis of plant tissues;
* partial elimination of volatile products;
* carbonization of cellulose;
* decomposition of glucosides and fats; and
* hydrolysis of proteins [18]

All of these reactions cause development of the characteristic coffee aroma; they are dependent both qualitatively and quantitatively on the method of roasting and the blend of coffee beans.[19] The unique combination of volatiles existing in coffee aroma has been the subject of several scientific studies which include several different techniques.

> Aishima and Ozawa (1989) used reversed phase HPLC to concentrate flavors compounds in aqueous systems. Tassan and Russell (1974) used head space analysis to determine volatiles from coffee brews, while Vitzthum and Werkhoff (1975) analyzed cycloalkylpyrazines in coffee aromas using gas chromatography-mass spectrometry (GC-MS) and nu-

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[18]Giovanni Fernaroly, Handbook of Flavor Ingredients. trans. and ed. Thomas Furia, and Nicolo Bellanca. (Cleveland, OH.: The Chemical Rubber, 1971). p. 793.

[19]Ibid., p. 794.

clear magnetic resonance(NMR) techniques. Ahimoda and Shibamoto (1990) also used GC-MS with head space analysis and identified 62 volatile compounds. Using instrumental methods, over 600 chemical compounds have been identified from roasted coffee beans.

Flament (1991) reported 18 general classes of flavor related materials from fresh ground coffee. These classes and the number of components in each were : 50 hydrocarbons, 20 alcohols, 28 aldehydes, 70 ketones, 20 acids, 29 esters, 8 lactones, 42 phenols, 99 furans, 26 thiphenes, 67 pyrroles, 27 oxazoles, 28 thiazoles, 13 pyridines, 79 pyrazines, 24 amines, 16 sulfides, and 9 miscellaneous compounds. While each component of chemical class contributes to the overall nature of coffee aroma, it is difficult to asses the relative significance of any individual component. Of the hydrocarbons and alcohols found in coffee, Gaudagni (1966) found that only terpenes are considered as contributing to coffee aroma. Furia (1975) on the other hand found that aldehydes impart a strong, fatty odor whereas the ketones, furans and lactones exhibit a fruity flavor and the phenols impart a smoky to burnt aroma. The presence of acids and sulfur-containing compounds are considered as imparting undesirable flavor notes ranging from sweet-like, to bitter and stale (Flament, 1991; Winter et al., 1972).[20]

Coffee and Aroma in the Mind of the Consumer: Psychology also plays a very important part on the acceptance of coffee by the consumer. It is important to take into consideration that flavor and aroma are elements that may influence the mind of the consumers and are determined by very personal experiences.

Recognition and association of aromas is a primitive and essential part of all animal and human life. Recognition usually implies associations and this is a very personal thing. Association may further imply continual use and habits which can be translated into condition-

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[20]Lee, et al. "Compositional Changes in Brewed Coffee as a Function of Brewing Time." pp. 1417-1419

> ing, custom and perhaps even ritual and tradition. The latter associations may stimulate emotions such as pleasure, disgust, anticipation and hate. In other words, aromas may produce important emotional effects on oneself or on others. Pleasant aromas are pinery, flowery, and spicy and may be associated with eating and sex. Unpleasant aromas are rotten, putrid and musty, and others associated with illness and death. Unfamiliar odors may be threatening until some association has been established. The distilled aromas from an oak or bay log campfire, or from a charcoal preparation usually involve pleasant associations. Cooking odors may be easily recognizable and pleasant. The aromas from roasting, grinding, or brewing coffee are usually pleasant experiences, even to children. Coffee aroma, particularly for adults, provides an anticipation of a friendly meal or coffee break.[21]

Permeation of Flavor and Aroma Volatiles: The actual tendency in the coffee industry and food industry to switch from packaging systems such as glass and metal, which are the only virtual flavor and aroma barriers, to more permeable plastic structures, raises questions about the need to understand the reasons why flavor and aroma may be lost from food while it is packaged. Two phenomena may occur: permeation of the volatile components through the plastic materials, or scalping (solution) of them into polymer structures.

Although the transport of gases and other low molecular weight particles through polymer films has been a challenging topic that has interested the scientific community for years, most of the studies have been focused on permeants such as oxygen, carbon dioxide and water vapor: even stan-

[21]Sivetz, Coffee Processing Technology. v.2 p. 63

dard methods to determine the rate transmission have been approved (ASTM E96/ASTM D3985). In contrast, the behavior of other organic permeants has been studied, but not as extensively, and there is still a lack of data available in this area.[22] Such a case is aroma and flavor of food. Their presence in the foodstuffs is on very low concentrations, sometimes less than one part per million). However their loss can dramatically affect the taste, and hence the perceived quality of the products. Losses can be because of broad removal of all flavors or of an imbalance caused by selective removal of only few flavor components.[23]

Scalping of Volatiles: Plastics are used as moisture barriers and also to serve as aroma barrier to prevent taint or absorption of undesirable foreign flavors and aromas by the products and to retain the original flavors in the food. Flavor and aroma molecules are susceptible to pass through plastic films and to scalp, or in other words, can be absorbed and trapped by the polymers from which the films are made.

Studies of scalping will help to determine the types of

[22]Ruben J. Hernadez, Jack R. Giacin, and A. Lawrence Baner, "Evaluation of the Aroma Barrier Properties of Polymer Films," in Plastic Film Technology. ed. Kier M. Finlayson. pp. 107-131.

[23]G. Strandburg, P.T. DeLassus, and B.A. Howell, "Thermodynamics of Flavors in Polymers."in Food and Packaging Interactions, Series 473. eds. Sara Risch, and Joseph Hotchkiss. p. 133

plastic films best suited for a particular application for food packaging. Although some films may be a good moisture or gas barrier for a product, that benefit can be offset by scalping. It is then necessary to reformulate the product in order to compensate for the loss of the flavor compounds into the package. The rate of volatile exchange and the point at which equilibrium is reached between the compound in the food and in the polymer must be known in order to reformulate the product successfully.

PACKAGING FOR COFFEE

The primary reason for packaging coffee is to deliver a unit weight in a fresh condition to the consumer. With any loss of freshness, the intrinsic value of the product is greatly diminished. For marketing purposes, packaging must be done as economically and attractively as possible. Beside describing the product, the package carries the supplier's name, the brand name, and sometimes the place of origin. Net weight and directions for preparation may be added on retail packages.

Package Requirements

A suitable package for coffee must meet the following requirements: low moisture-vapor transmission rate, excellent oxygen barrier characteristics, greaseproofness, impermeability to aromas and odors, slight permeability to carbon dioxide, durability (should withstand handling in distribution and at retail), ability to perform well on coffee package-forming and filling machinery, cost efficient. [24]

Types of Packages for Freshly Ground Coffee

There are three main types of packaging materials used to pack coffee: cans, flexible (paper, foil, and plastic films), and glass jars. The latter is mainly used for instant coffee.

Metal Cans: Vacuum packing in metal cans is the major method for ground coffee, since the can allows savings in manufacturing and distribution, larger customer inventories, smoother production schedules, and nationwide distribution by large manufacturers. This packaging method can protect ground coffee indefinitely if sufficient air is removed to produce a vacuum of 29.5 in. Hg or better.[25]

Flexible Packages: The replacement of metal cans by flexible packages in the United States has not been as important as it has been in Europe and South America. Nevertheless, there are several types of flexible coffee packages which have been recently introduced in the market.

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[24]Sivetz. v.l p. 520

[25]Wilmer A. Jenkins, and James P. Harrington, Packaging Foods with Plastics, (Lancaster, PA.: Technomic Publishing C., 1991). np.

* Brick-Type Packages: The most common structure used in brick packages is a heat-sealed lamination of PET/PE/Al foil/PE, having the PE act as a sealant. The Al foil acts as a gas barrier and the outer layer of polyester acts to puncture.

Brick type packages require that the coffee be held for four to six hours in a vented bin to allow most of the residual CO_2 to escape. The product is then packed in the foil laminate under a vacuum of 5 in. Hg producing a hard brick. CO_2 and some aroma constituents are lost during venting. However, freshness is unaffected when compared to the canned product because the package prevents the intrusion of oxygen during distribution.[26]

* One-Way Vent Valved Bag Packs: To avoid investment in intermediate storage between roasting and packaging, and to assure freshness of the freshly ground coffee, gases are vented by one-way valves attached to the walls of the bags. This allows CO_2 to escape but prevents the ingress of oxygen into the package since the valve is designed so that a small positive pressure differential always exists across it. As an alternative to this method, a small PE pouch that is permeable to CO_2, containing a mixture of calcium oxide and activated charcoal as a CO_2 absorber is sometimes used. There is no cost difference between these practices.

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[26]Jenkis, Packaging Food with Plastics. p. 191

New and Future Trends in Packaging for Coffee

Convenience for the producer, retailer, and consumer is the common characteristic that packaging developers use when looking for new packaging for coffee. All the different recently-launched new brands and redesigned ones make use of technological advances in packaging, trying to give more convenience for this product and to keep the interest of the consumer with more innovation than ever.

Pre-measured filter packs that eliminate the preparation steps to brew coffee at home using drip coffee makers, have been introduced in the market by Maxwell House. Coffee is being packed by high speed packaging machines, either in paper filter pouches or in gas flushed packages, by Co-Pack International. Also a Doy-pack or stand up pouch with resealable devices is being analyzed by different companies to pack coffee as a way to catch the attention of retailers and consumers at the shelf. [27]

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[27]Liz Fader, " Packaging Innovation for Profitability," Tea and Coffee Trade Journal.(January 1992) pp.82-89

PERMEABILITY, SOLUBILITY, AND DIFFUSION PHENOMENA

MASS TRANSFER OF GASES IN PLASTIC FILMS

The importance of transport behavior of gases and vapors in polymeric films has become very important with the accelerating development of highly impermeable or selectively permeable films for diverse applications in the food and pharmaceutical industries.[28] Product ingredients, gases, water, moisture, and packaging components, as well as atmospheric and environmental constituents are susceptible to permeate into and out of the product through the walls of the package. Thus, the knowledge of the permeation phenomena is of vital importance in selecting or developing polymeric materials to be used as packaging materials, especially when those will be used as barriers.

Contrary to glass and metal, polymers are prone to be permeated by many chemical elements and organic vapors. They may allow either contamination of products or contribute to degradation of them, if product components are lost to the outer surface when packed in plastic containers. However, in some cases, permeation could be an advantage, as when there is the need for slow delivery of drugs while applied on the skin, or when the material is selectively permeable to some elements. Permeability characteristics can be used to fit

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[28]Roy R. Chao and Sye S.H. Rizvi, "Oxygen and Water Vapor Transport Through Polymeric Film," in Food and Packaging Interactions, Series 365. ed. Joseph Hotchkiss. p. 218.

particular needs of the food industry, as in the case of produce which needs to breathe, to give off carbon dioxide and moisture, and to take in oxygen.[29,30] There are two types of mass transfer of gases and vapors: capillary flow and activated diffusion.

Capillary Flow Type, the elements pass through holes and pores on the surface of the material.

Activated Diffusion Type, permeation of a gas or vapor through a polymer material generally consists of solubilization of the penetrate into an effectively non-porous film at the inflow (upstream) surface, diffusion through the film under a concentration gradient, and release from the outflow (downstream) surface to the lower concentration side.[31]

DIFFUSION

Diffusion is the process by which mass is transported from one part of one system to another as a result of random molecular motions. The process can be visualized as a series of jumps of the penetrating molecules from one vaguely-

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[29] J. Comyn, Preface to Polymer Permeability. J. Comyn ed., (Essex, UK.: Elsevier Applied Science Publishers, 1986), V.

[30] Bracket, "Food Degradation." In Encyclopedia of Food Technology.

[31] Chao and Rizvi, "Oxygen and Water Vapor Transport Through Polymeric Film" in Food and Packaging Interactions, Series 365, p. 218

defined cavity to another in the polymer. The rate escalates with the increase of the number of cavities and the pressure and concentration of the permeate.[32] Diffusion of gases takes place readily; the rate of diffusion is proportional to the square root of the temperature and inversely proportional to the square root of the molecular weight. Thus, large permeants, tight polymers, and low temperatures lead to low diffusion coefficients.[33]

The diffusion coefficient is useful to describe how rapid is the motion of the molecules in the film and how much time is required to reach a steady state.[34] The diffusion coefficient is determined by the size and frequency of fluctuations in the openings between the polymer molecules. It is a combination of geometry and thermal effects. The diffusion coefficient is expressed almost universally in cm^2/s or m^2/s.

SOLUBILITY

The solubility coefficient is useful for describing the amount of aroma that will be absorbed by the package walls,

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[32]Chao and Rizvi, "Oxygen and Water Vapor Transport Through Polymeric Films." in Food and Packaging Interactions. Series 365. p.218

[33]P.T. DeLassus and G. Strandburg, "Flavor and Aroma Permeability in Plastics," in Food Packaging Technology, ed., Debra Henyon. pp. 64-73

[34]DeLassus et al., "Transport of apple Aromas in Polymer Films," in Food and Packaging Interactions, Series 365. Joseph H. Hotchkiss, ed., p. 14

and is typically expressed either as the number of parts by weight dissolved by 100 parts of solvents at specific temperature and pressure or as percentage by weight by volume[35]

$Kg.\ m^{-3}.\ Pa^{-1} = g.cm^{-3}.Pa^{-1}$

PERMEATION

Permeation is the mass transfer of a substance through a substrate, involving absorption on one surface, solution into the substrate, diffusion to the other surface and dissolution on the other side. Permeability is useful for describing the transport rate at steady state. The dimensions of permeability are mass (or volume) of permeant by path length by area^{-1} by time^{-1} pressure difference^{-1}. The more convenient units for use in packaging are: [36]

Engineering cc (or g).mil.100 square inches^{-1}d^{-1}.atm^{-1}

Metric cc (or g). 20 Um. m^{-2}. d^{-1}. atm^{-1}

It is important to bear in mind that there are different variables affecting the permeation rate, such as temperature, relative humidity, and concentration.

Temperature, most packages encounter different ranges

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[35]DeLassus et al., "Transport of apple Aromas in Polymer Films," in Food and Packaging Interactions, Series 365. p. 14

[36]Brown, Plastics in Food Packaging. p. 298.

of temperature during the distribution process. Higher temperature increase the transmission rate.

Relative Humidity, if a polymer is moisture sensitive, it may change the rate of permeation.

Concentration of Permeant, a higher concentration of permeant can lead to a higher sorption by the packages.[37]

The transmission rate is also inversely proportional to the thickness of the material. By doubling the thickness of the material, the transmission rate will be cut in half. However, economics plays a role in selection criteria, and here again it has raised the need to know the phenomena governing permeation theory for packaging materials.

CALCULATING PERMEABILITY, DIFFUSION, AND SOLUBILITY

The fundamental reason governing permeability of polymers is their relatively high level of molecular motion. Theoretical concepts state that diffusion (D) and permeability (P) values are obtained from permeability studies where the transport of a permeate through a polymer membrane is continually monitored (Isostatic Method)[38]. The process by which a small molecule permeates through solids

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[37]DeLassus et al., "Apple Aromas in Polymer Films," in Food and Packaging. p. 13

[38]Hernandez, et al. "Aroma Barrier Properties of Polymer Films," in Plastic Film Technology. pp. 110-131.

was first proposed by Graham in 1866. This model can be adapted to explain the permeation of gases or vapors through polymer films. It involves the following four stages.

* **Absorption** of the permeants molecules onto the surface of the polymer;
* **Solution** (scalping) of the gas or vapor into the polymer matrix;
* **Diffusion** through the wall along a concentration gradient; and
* **Desorption** from the other surface.

Permeability is then the product of the relation of the solubility coefficient and the rate of diffusion (D). Hence if any of the two coefficients are known, the third will be obtained by using the following equation:

$$P = D * S$$

Where:

P = Penetration

D = Diffusion

S = Solubility (scalping)

For this study, scalping will be defined as S = P/D

Diffusion can be described by using Fick's Laws. Fick's first law is the fundamental law of diffusion which can be applied to diffusion in the steady state, that is, where concentration does not vary with time. Other assumptions made in the simple treatment of permeation are that the concentration distance-relationship through the polymer is linear, and the diffusion takes place in only one direction. That is through the film with no net diffusion along or across it, which is the usual case for packaged products.[39]

Equations for the one-dimensional diffusion of substances in plane sheets, which can be assumed for most package calculations are given by Crank in his work *The Mathematics of Diffusion(1975)*. The first law predicts the flux of the permeant which will move across a unit surface area per unit time. Flux is proportional to the concentration gradient dC/dx in the direction of the movement. The negative sign of the equation, indicates that the permeant migrates to where the density is lower,[40] as it is explained in the following equation:

$$Fx = - D\ (dC/dx)$$

Where

Fx = Flux or amount of substance diffusion across unit area in unit time, in x direction.
D = Diffusion coefficient.
dC = Concentration Gradient.
dx = Distance or thickness of film.

The dimensions of diffusion can be deduced from this equation where x is the distance of the front from the

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[39]R.J. Ashley, "Permeability and Plastics Packaging," in Polymer Permeability. ed. J. Comyn. pp. 269-308.

[40]Ibid., pp. 269-308.

origin[41]

$$(\text{mass}/\text{length}^2 \cdot \text{time}) \equiv -D \left(\frac{\text{mass}/\text{length}^3}{\text{length}}\right)$$

or

$$D \equiv \text{length}^2/\text{time}$$

The diffusion coefficient, D, (also known as diffusivity) is dependent on the material, activation energy, and temperature. It is calculated from the composite constant D_0. The following equation is typical of the method used to determine the diffusion coefficient.

$$D = D_0 e^{-\Delta ED / R*T}$$

As diffusion proceeds to migrate toward areas of lower concentration the concentration changes. Fick's second law of diffusion relates the change in concentration with time to the instantaneous value of concentration.[42]

$$dC/dt = D(d^2C/dx^2)$$

[41]Brown, Plastics in Food Packaging. p. 297.

[42]J.Comyn, "Introduction to Polymer Permeability and the Mathematics of Diffusion," in Polymer Permeability. ed. J.Comyn. pp. 1-10.

PLASTICS AND PLASTIC FILMS

The subject of plastics and plastic films is already immense, intensively researched, and its growth has been increasing so quickly that it is necessary to select and condense much of the subject in order to keep it within the boundaries of this paper. It is necessary to narrow the topic only to films, and to those properties that affect the quality of the food products due to taint or loss of flavor and aromas.

Manufacture of Plastic Food Packages

The applications of plastics in the food industry are extensive. They are found as primary packaging structures such as pouches, bags, bottles, cans, trays, and tubes; seals, closures, and overwraps; labels, and tamper evident devices; as secondary packaging and components; and as tertiary packaging such as wraps around pallet loads of boxes and cartons.[43]

Plastic resins can be converted into the final product by different manufacturing processes[44]. High speed conversion to finished packages using the most economical structures is the dominant theme in modern plastic package

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[43]See attributes and plastics applications in appendix A

[44]See appendix A.

manufacture. Methods used for rigid containers include injection for precise finishes and shapes; thermoforming for high outputs and low tooling costs; and extrusion blow molding for bottles, irregular hollow shapes and handleware. For flexible packaging, the most common methods are extrusion, casting, and calendering. Some materials are also available in foam form.[45] Some other processes used by the film industry are coextrusion for combining structural and barrier layers; and coating and lamination for combining existing webs with thermoplastics and with dispersed materials such as latexes.[46]

PLASTIC FILMS

Most films are thermoplastic in nature, and can be made from most thermoplastic polymers. Films differ from each other in some key properties such as improved electric strength and flexibility, but are identical in all others. Both properties, electrical strength and flexibility, as well as many other properties, such as permeability, vary inversely with the film thickness.[47]

Plastic films come in several forms and formats that range from the low density polyethylene (LDPE) to high

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[45]Harper, Handbook of Elastomers and Composites. p. 1.80.

[46]Brown, Plastics in Food Packaging. p. 14

[47]Harper, Handbook of Plastics, Elastomers, and Composites. p. 1.81.

barrier polymers. The definition of polymer films varies, depending on quality and application. Most manufacturers recognize a main difference between sheets and films: film gauges are <250 Um (0.010 in or 10 mils).[48] Any material thicker than 10 mil is more properly called a sheet. However, there is a noticeable difference between the tolerances of thickness of the different kinds of plastic films. High-volume blown film, which is mainly used for carrying bags does not require the tightly controlled tolerances of cast films used for metallized snack packages.

Plastics Films Used in Packaging Food

In order to list the numerous applications of films in the food industry, it is necessary to break down the subject by considering the different plastics separately.[49] The versatility of plastics films also extends to the several types of packaging used in the food industry. In some cases, new packaging concepts in plastic films have been introduced, as in the case of shrink wrapping, and the range of form/fill/seal sachets and pouches.

High Barrier Polymers (HBP):

There is no standard for high barrier polymers in relation to gas and water vapor transmission. However

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[48]Muccio, Plastics Processing Technology. p. 87.

[49]See appendixes A.

commercial practice accepts as HBP those whose oxygen permeability limits are low enough to prolong significantly the shelf life of food products, and whose equivalent of oxygen transmission should not be greater than 1 cm^3*mil/(100 in^2*d*atm) at 23^0C at 50%rh.[50]

Recent practice, however, would place a dividing line at a tenth this amount. In fact, there is no universal barrier film. A high barrier polymer to oxygen may not be a high barrier to moisture or certain food components. Thus, high barrier packaging should also protect products from loss of volatiles; loss or gain of moisture; contamination; taint and penetration of solvents, odors, and flavor; scalping or absorption of flavor constituents by the package.

How much of a barrier level is required depends on the product, conditions of storage, transport and handling and on the shelf life and quality required. Despite all the qualities of HBP films, and although they appear to be satisfactory in the majority of the cases, many foods and beverages require more than one single layer material in order to be fully protected during their intended shelf life. Multilayers therefore, have assumed importance in food packaging. It is more economical to incorporate a thin layer of highly efficient barrier than it is to simply increase

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[50]Morris Salame, "Barrier Polymers." Wiley Encyclopedia of Packaging Technology. 1986.

the thickness of a monolayer material.[51] Therefore it is crucial to have adequate understanding of the interaction between foodstuffs and packaging materials. Also, due to the adoption of new technologies in food packaging, such as modified atmosphere and gas flushing, it is very important to study more efficient materials and barrier systems to design the proper barrier protection for the different food products.[52]

When selecting a barrier, it is necessary to keep in mind which factors the products have to be protected from and the mass transfer of the different food compounds, although the diffusion factors are usually more important than solubility in the case of flavor and aromas, and other transient molecules present in the foodstuffs, solubility must be considered first. It also must be determined if the polymer (solvent) has the capacity for absorbing food constituents (solute).[53]

The most important factor affecting mass transfer is the plastic's resistance to permeation, which in turn depends on the chemistry of the polymer. The chemical nature of the polymer is so powerful that it can out strip any other influence such as orientation. The barrier properties of film are partially dependent on the molecular

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[51]Brown, Plastics in Food Packaging. p. 301.

[52]Brown, Plastics in Food Packaging. p. 293.

[53]Ibid., p. 315.

characteristics of the polymer, and the inherent characteristics can often be enhanced by orientation.[54]

Factors Influencing Permeability in Plastics[55]

* Effect of chemical radical in the polymer chain
* Crystallinity and orientation of molecular chains
* Temperature above glass transition
* Thickness of layer
* Susceptibility to moisture
* Hydrocarbon content
* Additives

Some of the High Barrier Plastics Used in the Food Industry

Polyvinylidene Chloride (PVdC): PVdC's outstanding property is its low permeability to water vapor and gases. It is likely to be used as a component in coextruded film laminates because it can often supply adequate barrier properties at gauges too thin to be handled in unsupported film form. PVdC is a copolymer of vinylidene chloride and vinyl chloride that can be converted into film by casting or blow extrusion. The latter is preferred for the production of oriented film. PVdC films show a high crystallization rate at room temperature, therefore they must be oriented immediately after extrusion.

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[54]Ibid., p. 307.

[55]Brown, Plastics in Food Packaging. p. 307.

Oriented PVdC film is a clear film with good strength characteristics, particularly burst strength. It is heat sealable at fairly low temperatures (120-158^{0}C) but is not particularly stable when heated for any length of time above 60^{0}C. It has a high resistance to tear propagation but is difficult to handle on packaging equipment because of its limpness and "cling".

PVdC films cover a wide range of applications in food packaging for wrapping poultry, hams,cheeses and similar food products. Its outstanding low gas permeability makes these copolymers the ideal packaging material for vacuum packaging when the need of preventing bacterial growth and discoloration is required.[56]

Ethylene-Vinyl Alcohol (EVOH): The presence of the OH group in the EVOH resins is the principal key to their low permeability to gases such as oxygen, nitrogen and carbon dioxide. The outstanding gas barrier properties of EVOH copolymers make them suitable for gas-fill packaging techniques and in maintaining flavor and quality.

The gas and solvent barrier properties of EVOH polymers are reduced under humid conditions. However, because of the extremely low permeability, EVOH can be coextruded at very low gauges with other polymers.[57]

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[56]Brown, Plastics in Food Packaging. p. 132.

[57]Ibid., p. 133.

Nitrile Polymers: This family of polymers are better represented by a copolymer of acrylonitrile and methyl acrylate in the presence of a small amount of butadiene/acrylonitrile elastomer. This material is produced under the trade name of Barex. It has good clarity, good impact strength, and excellent gas barrier properties. It was originally developed for the soft drink industry.[58]

GAS CHROMATOGRAPHY TECHNICS

Gas chromatography is one method commonly used to determine the rate of gas/vapor permeability. Gas chromatography techniques separate the components of mixtures of volatile compounds and quantifies them. The basis for gas chromatographic separation is the distribution of a sample mixture between two immiscible phases. The separations of the different components of the mixture is accomplished by the differential adsorption or solution of the individual components between the two phases. One of these phases is *stationary* while the second is *mobile*, which consists of a inert gas or gas carrier that sweeps the individual components at different rates through the stationary phase, depending upon their relative distribution or partition between the two phases. Gas chromatography methods are widely used by many laboratories and research institutions to find the permeability of the different

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[58]Briston, p. 355

packaging materials because they give quantitative analysis, and variations in the percentage composition of the gases can be detected, and also because the interpretation of the data is simple.[59]

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[59]R. Alan Jones, An Introduction to Gas-Liquid Chromatography. (London : Academic Press Inc., 1970). n.p

Chapter 3

METHODOLOGY

THE CONCEPT OF THE EXPERIMENT

Several scientific studies have been carried out on the transmission rate of low molecular weight gases in polymer films. Typically, the measurement value is of the steady state permeation rate. However, in this study, the major concern is the solubility coefficient (scalping values of the packaging materials with respect to the coffee aroma), and the diffusion coefficient. The first is a thermodynamic parameter, and the latter a kinetic parameter. Therefore, in order to achieve reliable results, it is necessary that a system monitor the permeant's behavior regularly, obtain precise and consistent data, and be able to analyze and interpret it.

In order to simplify the experiment, it was decided to work with only one of the over 600 compounds identified in coffee aroma. It was further recognized that no laboratory equipment is currently available to match the sensitivity of the human nose. Nevertheless, it was assumed that any compound that was volatile enough to be analyzed on a gas chromatograph would give reliable values for the experiment.

The information obtained from analyzing the chosen compound at its highest concentration level while in interaction with the polymeric film samples would be correlated with the values of the same compound obtained from analyzing the aroma of fresh roasted ground coffee in interaction with new samples of the same films. This was a simple comparative test which gave straightforward results. It was thought that if it were possible to obtain measurements of the selected compound at low levels, which only sensory tests were able to perceive, then it would also be possible to make sure the values were accurate and reliable. When these values were interpreted quantitatively by a computer, they would show the barrier performance of the tested materials in relation to the compound, and then the most suitable material for packaging coffee could be identified.

EXPERIMENT PREPARATION

The following equipment and materials were required for the experiment:

- MAS 2000 Organic Permeation Detector System
- 486 SX Computer
- Nitrogen high purity
- Hydrogen high purity
- Pyridine 99.9% HPLC grade
- Recently roasted coffee grounds
- Film Samples (3 different materials)
- Paperboard film holders
- Gas tight syringes 0.025 cc

Selection of Sample Volatile

Two parameters were of critical importance in the selection of the gas permeant. One, its presence in the coffee aroma had to be easily identifiable, and, two, it had to be highly volatile for detection by the gas chromatograph. Pyridine, a compound with a strong smell whose burnt-like odor is easily perceived in highly roasted coffee, was selected. Thirteen pyridine compounds have been identified in coffee. They are found in the basic fraction of food volatile, and are the result of thermal degradation of trigonelline.[1] The organoleptic properties of the pyridine group are associated with flavor qualities such as: green, bitter, burnt, astringent, hazelnut and rum-like. Data related to caffeine content of this component indicates pyridine presence in both green and roasted coffee.[2]

Preliminary testing was done to verify the relationship between coffee grounds and pyridine by personnel of MAS Technologies at their facilities. The results obtained seemed very reliable and indicated that the permeation values differed by a factor of 400, showing that the concentration of pyridine in coffee grounds is approximately 400 times smaller than a full vapor pressure at room temperature.

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[1]Flament, "Coffee, Cocoa, and Tea." In Volatile compounds in Foods and Beverages. pp. 617-671.

[2]Heat, Source Book of Flavors. p. 165.

Selection of Film Samples

Three polymeric films were selected for this experiment. Two are commonly used in the food industry as high barrier packaging materials. They were chosen as materials for comparison with Barex^R 210, an acrylonitrile methylacrylate copolymer. It is important to point out that the materials are flexible films which were coated to enhance their barrier properties. The Barex^R film samples, however, had not been modified at all. Therefore, the values obtained from Barex could be improved through either coating or laminating to other materials.

Bicor$^{(R)}$70 MET-HB: This is an oriented polypropylene vacuum metallized film with high barrier properties. It is used as outer web of laminations.[3]

Bicor$^{(R)}$ 84 AOH: This is a two-sided, oriented polypropylene film, acrylic coated on one side and PVOH coated on the other. This film is used only as the outer web of lamination, having the PVOH surfaced buried. The film is designed for gas flushing applications, and is excellent at maintaining initial gas concentration levels. It also provides superior flavor and aroma barriers.[4]

[3]See appendix C.

[4]See appendix C.

Barex(R) 210: This is a high barrier film used in the food packaging of products which require retention of aroma and flavor to ensure freshness. Particular interest should be given to its antiscalping properties. It also can be used for gas flushing packaging to extend shelf life of products.[5] For the experiment purposes, was used a monolayer film of Barex^R 210, an impact modified acrylonitrile methylacrylate copolymer.[6]

Selection of Equipment

A MAS 2000 Organic Permeation Detector was used to determine the permeability rate, the diffusion rate, and the solubility values of pyridine, and to correlate them with the values obtained from the volatile compounds of fresh ground coffee.

The MAS 200 is a state-of-the-art instrument capable of detecting compounds in the low parts per billion range (ppb) in a significantly short time frame. It represents the most sophisticated and cutting-edge technology available in packaging research at this time. It incorporates diffusion theory in real time to obtain estimates of permeability and solubility from the early portion of the permeation curve, well before steady state values are achieved.

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[5]British Petroleum, Technical Catalog about Barex Polymers.

[6]See appendix C.

The system uses an isostatic test method and incorporates a flame ionization detector (FID), precise temperature and flow rate control. The whole system is regulated by a computer driven by a comprehensive software package, which allows for constant monitoring of the permeation rate of the permeant through the polymer membrane. It processes the acquired measurements and data, and then renders valuable information in regard to numerous packaging issues, such as:

Scalping: It calculates how much of the organic compounds will be absorbed by the films.

Permeation: It identifies the permeation values of a material with respect to a particular flavor or ingredient.

Curing rates: It predicts the expected curing rates of a film or material after it has been produced or printed.

THE SOFTWARE PACKAGE[7]

The permeation theory used by the MAS 2000 is based on Fick's First Law as well as Henry's Law. The steady state permeation coefficient P is also assumed to be directly proportional to a material's solubility coefficient S and its diffusion coefficient D. The following formula shows

[7]Technical Manual MAS 2000

this relationship:

$$P = D * S$$

The solution to the differential equations describing the mass transport rate through the planar surface is:

$$R_t = R\ C^{1/2}\ \text{Sum}\ [\exp\ (-k^2\ C)]\ \text{for}\ k = 1,3,5\ ....$$

R_t is the mass transport rate time t
R is a constant associated with the permeation coefficient.
C is a constant associated with the diffusion coefficient.
R and C are defined by the equations :

$$R = 4\ P\ /\ pi^{1/2}$$

where P is the permeation coefficient.

$$C = 1\ /\ (4\ D\ t)$$

where t is time and D is the diffusion coefficient.

In the experiment associated with the solution to this equation, other parameters need to be considered:

B, which is the initial baseline value associated with the organics trapped in the material and which are desolving from the material at a steady state the test is initiated.

t_p, which is the time associated with the initiation of the test. This parameter is usually known only approximately due to instrumentation lag time. Therefore, the equation to be solved is :

$$R_t = B + R\ C^{1/2}\ \text{Sum}\ [\exp\ (-k^2\ C)]\ \text{for}\ k = 1,3,5\ ....$$

where $C= 1/[4D(t-t_0)]$ and $R = 4P\ /pi^{1/2}$

The solution to this equation involves 4 parameters

B = the baseline value
P = the permeation coefficient
D = the diffusion coefficient
t_0 = the test initiation time

THE EXPERIMENT PROCEDURE

The operation of the MAS 2000 Organic Permeation Detector was very similar to a permeation apparatus described in *The Evaluation of the Aroma Barrier Properties of Polymer Films*.[8] A schematic diagram of the isostatic equipment can be found in Appendix B. The vertical permeability cell is made of aluminum. It is conformed by two moving plates that displace horizontally; each plate is equipped with inlet and outlet valves. A rectangle of 6" * 6.5" is cut from the film to be tested and framed by two fiberboard film holders of the same size as the film sample and with a 4" diameter perforation. Care was taken to make sure that each sample came from the same piece of material provided by the manufactures. The sample is then inserted by mounting the framed film between the two aluminum plates, forming two low cell chambers. Each cell is separated from each other by the film, which is acting as a membrane. The barrier layer faces the back of the unit towards the detector. The surface of the film holders remain outside of the opening of the plates, so the fiberboard does not affect the permeation of the film. Each chamber has a volume of 12.9 cc. Leakage is prevented by the isolation of the chambers from each other. This is achieved by the compression of an elastomeric Viton "O" ring in the front cell chamber.

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[8]Hernandez et al., in Plastic Film Technology. Ed. Finlayson pp. 107-131

Once the system is on, the valves of the gas cylinders are opened and set to the proper pressure to control the flow rates. Then, the system requires input related to parameters and measurements of the samples. The test is ready to begin and the gas line valves automatically open and gases start to circulate throughout the system to assure full vapor pressure at test start. Initially, the permeant gas is vented via the exhaust port on the side of the chassis of the apparatus. Nitrogen is flushed through both sides of the test cell, hydrogen and air are flushed to the detector, and air is sent to the cell closure system. At this stage, the sample is placed between the cell plates, and it is closed. Prior to igniting the detector, the back cell, the plumbing interfacing the cell, and the sampling valve are purged of residual permeant vapor.

After a steady baseline is established on the screen, it is saved in the computer memory as 0 value reference. Now, it is appropriate to calibrate the MAS 2000 by using the gas
tight syringe via the injection port on the top of the cover of the chassis. It is injected with 0.025 cc of 99.9% pure pyridine. The computer compares the resulting signal response with the known number of molecules of permeant in the syringe injection. This value is saved in the permeant parameters screen of the test parameters and measurements section of the program. Calibrations conducted from the

actual test gas mixture may be highly unreliable due to the additional variable of gas flow rate and the time to steady state concentration.

The system is purged again. When the signal has dropped back to the original steady baseline value, the system will automatically exit the calibration mode and the actual test begins. Internal valves will activate, and, this time the organic test vapor is routed from the exhaust to the test cell and against the material sample. The permeate vapor is introduced into the cell via nitrogen flushing.

The cell temperature is kept steady by FID control with two electric heaters, and a constant concentration of organic permeant vapor continually flows through the front cell chamber. Simultaneously, a constant flow of nitrogen is passed through the front cell removing permeant molecules from the front cell at a constant rate and conveying it to the detector apparatus. This detection system consists of a flame ionization detector (FID), interfaced to the permeability cell via a computer aided gas sampling valve. At preselected time intervals the concentration of penetrant in the nitrogen stream flowing through the back cell is determined, and the transmission rate is monitored continually until steady state conditions are attained. The computer compares the resulting signal response with the data obtained during calibration, and the permeation results are plotted on the screen. The computer calculates the signal, which is detected by the FID in terms of pico-amps, and converts it in terms of micro-grams/m^2.hr.

The whole experiment requires at least 2 film samples of each material, in interaction with both, the pure pyridine and the headspace obtained from coffee grounds. Different temperatures were required for each sample of each material. Overall there were 9 repetitions of these procedures for the testing of pyridine and 8 for the testing of coffee aroma.

Since the MAS 2000 is able to project to room temperature the permeation values obtained at different temperatures, it was then assumed that the temperature range was not necessary to maintain at the same level for every set of testings. Therefore, the conditions were changed to levels at which the values were significantly different from the results of the prior testing. See Table #1 (page 70)

A constant concentration of vapor of pyridine is obtained using a midget bubbler to bubble nitrogen gas through the liquid permeant. A fume hood is required. The aroma from the coffee grounds is obtained by passing nitrogen gas through a drying tube containing the grounds and channeling the resulting vapor into the cell of the MAS 2000. To obtain a lower vapor concentration, the permeant vapor stream is mixed with another stream of pure carrier gas. Before being directed to the permeation cell, the vapor stream is passed through a glass reservoir as a means of dampening disturbances. The vapor generator system was mounted in a constant temperature water bath, and is maintained at 1^0C above ambient temperature to avoid condensation after the permeant vapor passed through the glass reservoir. The permeant vapor concentration is expressed throughout as ppm (v/v,mg/l) vapor in nitrogen. Flow meters were used to provide a continuous indication that a constant rate of flow was maintained. Gas flows were regulated with needle valves.

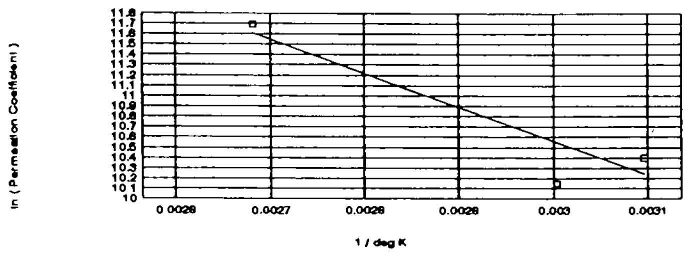
TABLE # 1
TEMPERATURE CONDITIONS

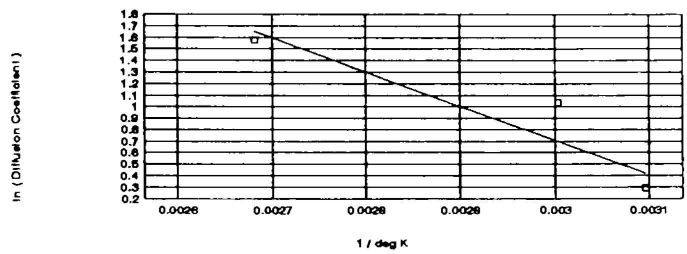
MATERIAL	PERMEANT	TEMPERATURE CONDITIONS
BICOR^R 84 AOH	PYRIDINE	80^0C 90^0C 100^0C
	COFFEE	100^0C 110^0C
BICOR^R 70 MET-HB	PYRIDINE	50^0C 60^0C 100^0C
	COFFEE	50^0C 60^0C 100^0C
BAREX^R 210	PYRIDINE	60^0C 80^0C 100^0C
	COFFEE	60^0C 100^0C 110^0C

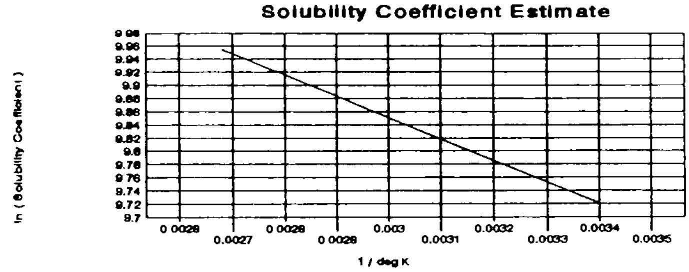
FIGURE # 1
Projection to Room Temperature
.7 mil Bicor[R] 70

Permeant:	*pyridine*
Concentration:	*1.00*

Permeation Units:	*ugms/m2.hr*
Diffusion Units	*1/hrs*
Solubility Units:	*ugms/m2*







Arrhenius Fit
Regression Parameters
ln(P) = int. + slp. / T

	Intercept	Slope
Permeation	*20.40968*	*−3283.85*
Diffusion	*9.584235*	*−2958.94*

Arrhenius Fit
Room Temperature Projection (20 deg. C)

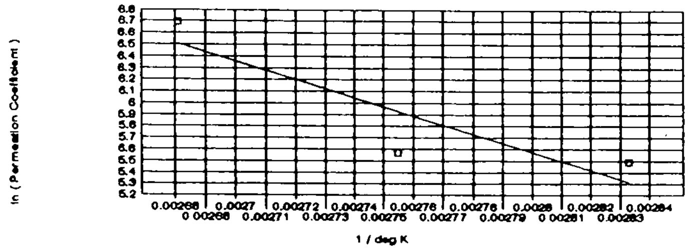
Permeation	*10699.52 ugms/m2.hr*
Diffusion	*0.640138 1/hrs*
Solubility	*16714.37 ugms/m2*

FIGURE # 2
Projection to Room Temperature
.8 mil Bicor[R] 84

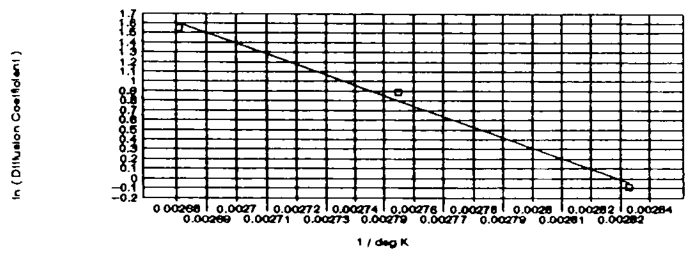
Permeant:	*pyridine*
Concentration:	*1.00*

Permeation Units:	*ugms/m2.hr*
Diffusion Units	*1/hrs*
Solubility Units:	*ugms/m2*

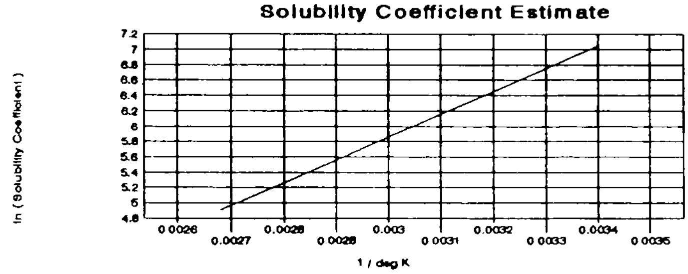
Permeation Coefficients



Diffusion Coefficients



Solubility Coefficient Estimate



Arrhenius Fit
Regression Parameters
ln(P) = int. + slp. / T

	Intercept	Slope
Permeation	*27.53321*	*−7842.20*
Diffusion	*30.56888*	*−10805.8*

Arrhenius Fit
Room Temperature Projection (20 deg. C)

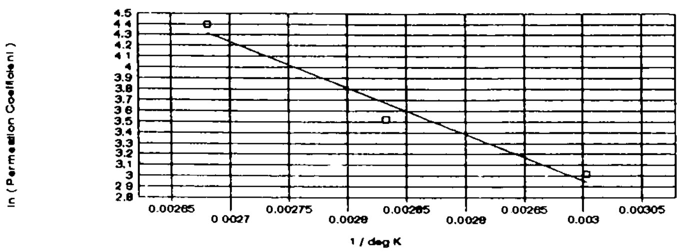
Permeation	*2.584359 ugms/m2.hr*
Diffusion	*0.002331 1/hrs*
Solubility	*1108.316 ugms/m2*

FIGURE # 3
Projection to Room Temperature
1.0 mil Barex[R] 210

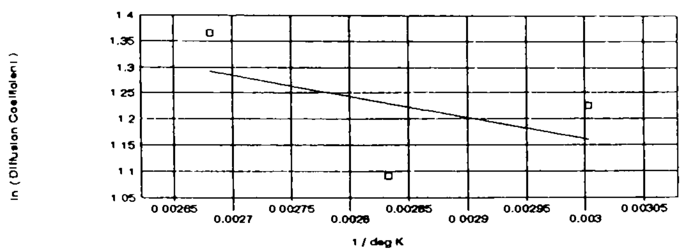
Permeant:	*pyridine*
Concentration:	*1.00*

Permeation Units:	*ugms/m2.hr*
Diffusion Units	*1/hrs*
Solubility Units:	*ugms/m2*

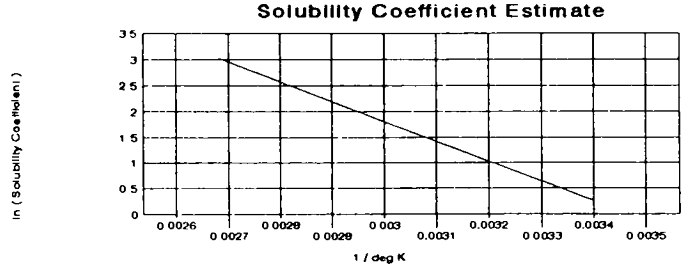
Permeation Coefficients



Diffusion Coefficients



Solubility Coefficient Estimate



Arrhenius Fit
Regression Parameters
ln(P) = int. + slp. / T

	Intercept	Slope
Permeation	*15.78085*	*−4274.86*
Diffusion	*2.399123*	*−412.748*

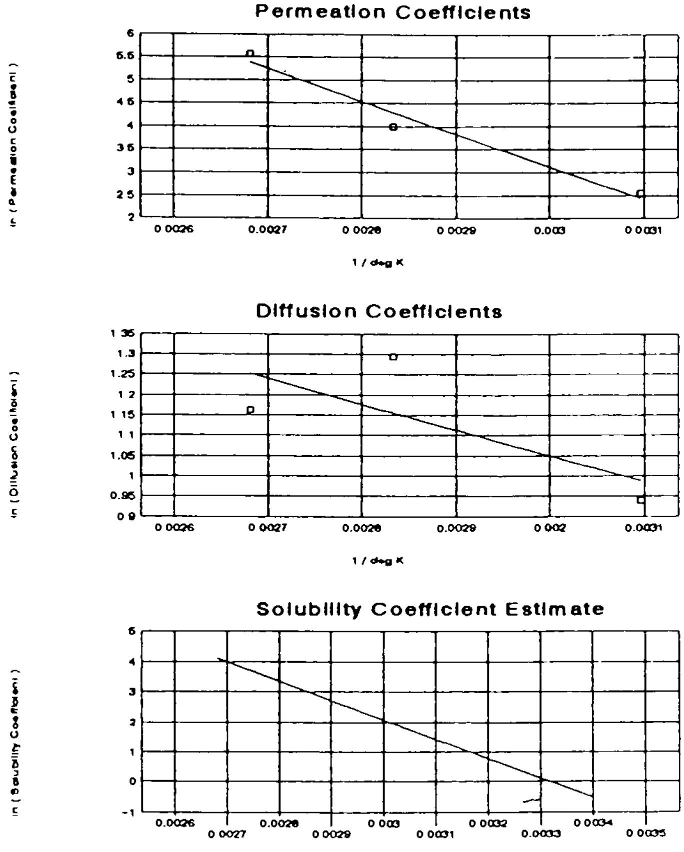
Arrhenius Fit
Room Temperature Projection (20 deg. C)

Permeation	*3.632032 ugms/m2.hr*
Diffusion	*2.718211 1/hrs*
Solubility	*1.336184 ugms/m2*

FIGURE # 4
Projection to Room Temperature
.7 mil Bicor® 70

Permeant:	coffee
Concentration:	1.00

Permeation Units:	ugms/m2.hr
Diffusion Units	1/hrs
Solubility Units:	ugms/m2



Arrhenius Fit
Regression Parameters
$\ln(P) = \text{int.} + \text{slp.} / T$

	Intercept	Slope
Permeation	24.4118	-7098.03
Diffusion	2.948313	-632.776

Arrhenius Fit
Room Temperature Projection (20 deg. C)

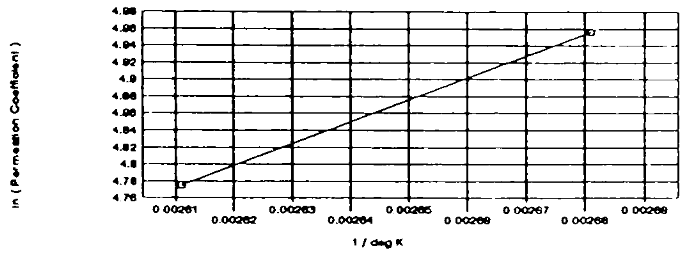
Permeation	1.419996 ugms/m2.hr
Diffusion	2.232915 1/hrs
Solubility	0.635938 ugms/m2

FIGURE # 5
Projection to Room Temperature
.8 mil Bicor[R] 84

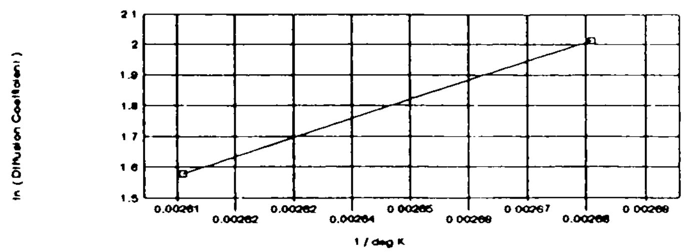
Permeant:	*coffee*
Concentration:	*1.00*

Permeation Units:	*ugms/m2.hr*
Diffusion Units	*1/hrs*
Solubility Units:	*ugms/m2*

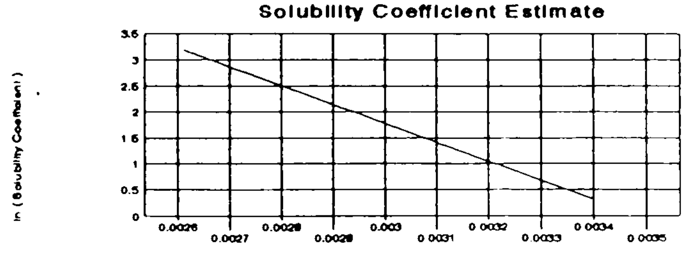
Permeation Coefficients



Diffusion Coefficients



Solubility Coefficient Estimate



Arrhenius Fit
Regression Parameters
ln(P) = int. + slp. / T

	Intercept	Slope
Permeation	*-1.96746*	*2582.345*
Diffusion	*-14.6947*	*6232.015*

Arrhenius Fit
Room Temperature Projection (20 deg. C)

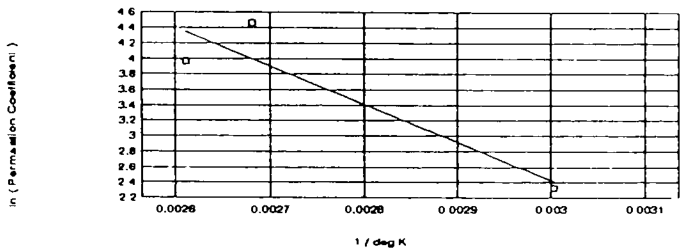
Permeation	*885.5844 ugms/m2.hr*
Diffusion	*620.6110 1/hrs*
Solubility	*1.426955 ugms/m2*

FIGURE # 6
Projection to Room Temperature
1.0 mil Barex[R] 210

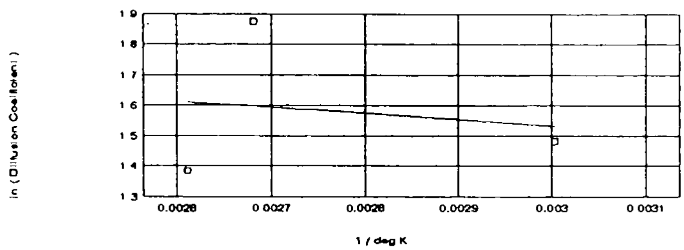
Permeant:	*coffee*
Concentration:	*1.00*

Permeation Units:	*ugms/m2.hr*
Diffusion Units	*1/hrs*
Solubility Units:	*ugms/m2*

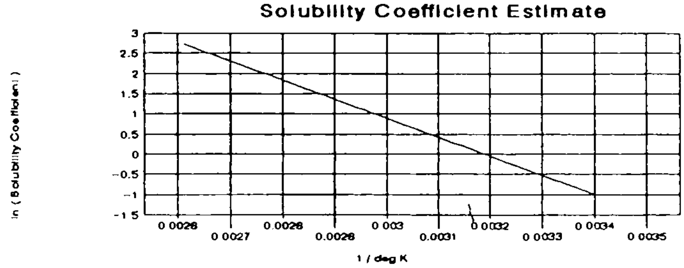
Permeation Coefficients



Diffusion Coefficients



Solubility Coefficient Estimate



Arrhenius Fit
Regression Parameters
ln(P) = int. + slp. / T

	Intercept	Slope
Permeation	17.22989	-4934.72
Diffusion	2.142107	-203.405

Arrhenius Fit
Room Temperature Projection (20 deg. C)

Permeation	1.652047 ugms/m2.hr
Diffusion	4.274196 1/hrs
Solubility	0.386516 ugms/m2

Data Collection and Analysis

The main advantages of the MAS 2000 Organic Permeation Detector are that it facilitates the testing procedures, it collects and analyzes the data efficiently and with high speed, and it requires low involvement from the user. The software package automatically makes all the needed calculations and reports comprehensive results in a very sensible and clear way. The time required by the equipment for parameter.measurements, control, and data analysis is about 5 seconds. The number of FID detector samples averages 10.000 per cycle.

The collected data is analyzed according to a non-linear regression which requires an average of 30 points to fit them into the Fick's law of planar surface.

Chapter 4

ANALYSIS AND DISCUSSION OF RESULTS

Restatement of Objectives

The main purpose of this study focused on two topics: the permeation and scalping of acrylonitrile copolymers while they are in interaction with pyridine and roasted ground coffee. The solubility factor is considered to be a mesurement of aroma scalping.

A summary of the results of the experiment can be seen in the following table. The full set of the results is shown in the Figures 1 to 6.

TABLE # 2
PROJECTION OF VALUES TO ROOM TEMPERATURE

PERMEANT : PYRIDINE				
FACTOR	MATERIAL			UNITS
	BICOR^R 70	BICOR^R 84	BAREX^R 210	
PERMEATION	10699.52	2.584359	3.632032	ugms/m^2.hr
DIFFUSION	0.640138	0.002331	2.718211	1/hrs
SOLUBILITY	16714.37	1108.316	1.336184	ugms/m^2
PERMEANT : COFFEE VAPOR				
PERMEATION	1.419996	885.58444	1.652047	ugms/m^2.hr
DIFFUSION	2.231915	620.6110	4.274198	1/hrs
SOLUBILITY	0.635938	1.42669	0.386516	ugms/m^2

Reliability of the Results.

After calibration, it was possible to demonstrate some points of interest about the experiment :

1. The MAS 2000 detected transmission of pyridine in both set of testings : when it is used 99.9% pure and in the coffee aroma.

2. When calibrating the testing equipment, the calibration was done using 0.025 cc of 99.9% of pure pyridine. The results were reported in terms of micro-grams/m^2.hr. Since the coffee aroma is a complex compound, then a more accurate unit could be micro-moles/m^2.hr for the actual measurements that were done on the permeation of coffee aroma.

3. The previous point demonstrates that the MAS 2000 is able to detect highly volatile molecular compounds in ranges as low as those present in the coffee aroma.

Conclusions with Respect to Stated Objectives of the Study

According to the results given by the MAS 2000, the following are some findings with respect to the objectives of the research :

1. according to the results in table # 2, Bicor^R 84 is a better barrier than Bicor^R 70 and Barex^R 210 when in interaction with pyridine.

2. The values obtained for the permeation rates of Bicor^R 84 are not consistent in relation with the values obtained for the other two films. The rate is significantly lower for this material while in interaction with pyridine than when in interaction with coffee. This fact is contrary to the theories on which this study is based: a higher concentration of the permeate can lead to a higher sorption by the packages.[1]

3. A potential source of error was present in the trial of Bicor^R 84 at 100^{0}C, because the values are slightly higher than the ones at 110^{0}C. (See Appendix C) This fact also is opposite to the diffusion theory which says that diffusion of gases takes place readily; the rate of diffusion is proportional to the square root of the temperature and inversely proportional to the square root of the molecular weight. Thus, large permeants, tight polymers and low temperatures lead to low diffusion coefficients.[2] (See page 43)

3. The difference in permeation values between Barex^R 210 and Bicor^R 70 while in interaction with coffee aroma, does not represent a meaningful difference in terms of barrier packaging systems for food.

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[1]DeLassus et al., "Apple Aromas in Polymer Films," in Food and Packaging. p. 13

[2]P.T. DeLassus and G. Strandburg, "Flavor and Aroma Permeability in Plastics," in Food Packaging Technology, ed., Debra Henyon. pp. 64-73

4. The degree of permeation of the three materials is very low at the projected 20^{0}C of temperature. Thus, all the materials should be considered as high barrier materials.

5. The diffusion rates of all three materials increased when in interaction with the coffee aroma.

6. The degree of scalping (solution) of the three films, Barex^R 210, Bicor^R 84 and Bicor^R 70 are at extremely low levels. Thus, they do not represent a meaningful difference with regards to food packaging.

7. The scalping (solution) of Barex^R 210 is lower when compared to that of Bicor^R 84 and of Bicor^R 70. Therefore, it can be concluded that Barex^R 210 has better anti-scalping characteristics than Bicor^R 84 and Bicor^R 70. However, it is also necessary to say that the results of the testing of coffee aroma could have been misleading by any type of error due to the small units of the results.

8. The diffusion rates of Barex^R 210 are higher than the other two films. Refer to Table # 2 (page 72).

Potential Sources of Error

The potential sources of error could be of different types, such as : pinholes on the films, scratches on the surface of the films, malfunctioning of the equipment, and even human factors. Especial concern is about points # 1 and 2, where discrepant results can mislead to any conclusion. An additional area of concern is the action of relative humidity as co-opermeant during testing. The MAS 2000 does not require conditioning of the films nor the laboratory in order to run the trial.

General Conclusions

* The aroma barrier efficiency of acrylonitrile methylacrilate copolymers (Barex^R 210) has been verified. Refer to Table # 2. They have a range of performance similar to that of other high barrier packaging materials available in the market. Because of the combination of permeation and scalping properties, these materials should be of particular interest to the food industry, especially when packing high volatile compounds.

* Acrylonitrile Methylacrilate copolymers present high potential to be used as inner layers of pouch packages for coffee products. The copolymers could be combined with thin layers of less expensive materials and enhance their barrier properties at a reasonable cost.

* The diffusion results of the trials on the coffee grounds were affected by the several other compounds present in the coffee aroma.

Recommendations for Future Study

1. In order to verify the accuracy and reproduction of the results, this study should be repeated under similar conditions. Organoleptic tests should be also conducted to

corroborate the results obtained by the MAS 2000 with standards already accepted by the industry.

2. The flame ionization detector (FID) detects the diffusion rates and permeability values of the materials, and solubility is calculated by the MAS 2000. Therefore, other type of testing methods such as analytic or mass spectrometric, should be conducted in order to correlate the solubility values.

3. The ASTM list several methods to evaluate transmission of moisture, oxygen, carbon dioxide, and other large molecular gases. If there were a demonstrable repetition of the results obtained during the experiment described in chapter 3, then there would be the possibility that this would become a standard for the evaluation of transmission of low molecular weight gases through polymer films.

4. Further research is necessary to find the compatibility of coffee with the different high barrier polymer films available in the market. The copolymers of acrylonitrile methylacrylate offer high potential to become the innerlayer of the film structures for packing aromatic products. Additional research will also be necessary to test the level of permeability of these structures and to find the minimum gauges of the films to maintain the quality of the products during the expected shelf life.

5. The present study could be repeated taking into account several procedures to avoid error in the results,

such as:

* The rate of variation of permeability of different films could be proved by using the same permeant at different concentrations at the same temperature conditions.

* To evaluate the permeation and scalping of packaging films for the aroma of a natural food product as complex as coffee, it is necessary to separate and identify the diverse components, and evaluate one by one, particularly those which are correlated with coffee flavor and aroma.

* Another alternative could be to calibrate the MAS 2000 with the headspace of the product (coffee) and evaluate a specific film with the whole volatile mix of the product. Thus, the conclusion would be the permeation rate with respect to the whole product.

BIBLIOGRAPHY

Academic Encyclopedia Americana, 1994 ed., s.v. "Diffusion," by George Gorin.

Achtert, Walter S. The MLA Style Manual. The Modern Language Association of America. 1985.

Bakker, Marilyn. ed. The Wiley Encyclopedia of Packaging Technology. John Wiley & Sons. New York, 1986., s.v. "Nitrile Polymers," by Joseph P. McCaul.

Briston, John H. Plastic Films. 3th ed. Longman Scientific & Technical. Essex, UK., 1989.

Brown, William E. Plastics in Food Packaging. Properties, Design, and Fabrication. Marcel Dekker Inc. New York, 1992.

Crank, J. The Mathematics of Diffusion. 2nd ed. Clarendon press. Oxford, UK., 1983.

Comyn, J., ed. Polymer Permeability. Elsevier Applied Science Publishers Ltd. Essex, UK., 1986

Denney, R.C. A Dictionary of Chromatography. 2nd. ed. John Wiley & Sons. New York, 1982.

Ebergard, William, Henry F., Holtzclaw, and W. R. Robinson. College Chemistry. Qualitative Analysis. 6th ed., D.C. Heath and Co. Lexington, MA

Fader, Liz. "Packaging Innovation for Profitability." Tea and Coffee Trade Journal. January 1992. pp. 82-89.

Fernaroly, Giovanni. Handbook of Flavor Ingredients. Trans. Thomas E. Furia and Nicolo Bellanca. The Chemical Rubber Co., Cleveland, OH., 1971

Finlayson, Kier M., ed. Plastic Film Technology. High Barrier Films for Packaging. Technomic Publishing Co., Inc. Lancaster, PA., 1989.

Goerne, Carrie. "Coffee Consumption Down but Sales of Exotic Blends Pick up." Marketing News. July 20 1992. p. 22

Guise, W. "Organoleptics and Packaging Materials." Packaging, August 1991, pp. 4-8.

Harper, Charles A., ed. Handbook of Plastics, Elastomers, and Composites. 2nd. ed. McGraw-Hill, Inc. New York, 1992.

Heat, Henry B. Source of Food Flavors. The AVI Publishing Co., Westport, CT. 1981.

Henyon, Debra K., ed. Food Packaging Technology. ASTM STP 1113. American Society for Testing Materials. Philadelphia, 1991.

Hotchkiss, Joseph H., ed. Food and Packaging Interactions. American Chemical Society. Division of Agricultural and Food Chemistry III. ACS Symposium Series 365. Meeting 193rd. Denver, CO., 1987.

Hui, Y.H., ed. Encyclopedia of Food Technology. John Wiley & Sons. New York, 1991

Jenkis, Wilmer A., and James P. Harrington. Packaging Foods with Plastics. Technomic Publishing Co., Inc. Lancaster, PA., 1991

Kadoya, Takashi, ed. Food Packaging. Academic Press Inc. San Diego, CA., 1990.

Lee, Terrence A., Rebecca Kempthorne, and James K. Hardy. "Compositional Changes in Brewed Coffee as Function of Brewing Time." Journal of Food Sciences. 57, No. 6, 1992. pp. 1417-1419.

Lester, James D. Writing Research Papers. A Complete Guide. Harpers Collins. New York, 1993.

Littlewood, A.B., Gas Chromatography. Principles, Techniques, and Applications. 2nd ed. Academic Press Inc. New York, 1970

Maars, Henk. Volatile Compounds in Foods and Beverages. Marcel Dekker Inc. New York, 1991.

Masterson, Peg. "Top 100 Succumbs to Specialty Coffees Aromas." Advertising Age. September 29, 1993. pp. 30-34.

Maxwell Jr., John C. "Specialty Coffee Sales Perking in Flat Market." Advertising Age. June 14, 1993. pp. 46.

Muccio, Edward A. Plastic Processing Technology. ASM International, Materials Park, OH., 1994.

Risch, Sara J., and Joseph H. Hotchkiss, eds. Food and Packaging Interactions. American Chemical Society. Division of Agricultural and Food Chemistry. IV. ACS Symposium Series 473. Meeting 200th. Washington, D.C., 1990.

Rogers, Allison. " No Break for Coffee Prices." Fortune. June 13, 1994. pp. 13

Sacharow, Stanley, Roger C. Griffin. Principles of food Packaging. 2nd ed. AVI Publishing Co. Westport, CT., 1980.

Sivetz, Michael. Coffee Processing Technology. 2 vols. The AVI Publishing Co., Inc. Westport, CO., 1963.

Sugden, Virginia M. The Graduate Thesis. The Complete Guide to Planning and Preparation. Pitman Publishing Co. New York, 1973.

Yang, Dori Jones. "Trouble Brewing at the Coffee Bars." Business Week. August 1, 1994. pp. 62.

APPENDIX A

PLASTICS IN FOOD PACKAGING

PRINCIPAL METHODS USED IN MANUFACTURING FOOD CONTAINERS OF PLASTICS[1]

INJECTION MOLDING	Plastics are melted in a cylinder, injected under pressure of a confined piston into matched, closed molds, and cooled to provide the finished shape.
INJECTION BLOW MOLDING	Plastics are injection molded as above, then transferred in-line or to a separate line for expansion by gas pressure into a larger shape. Injection blow molding provides the means to create "re-entrant" containers, I.e., those with a neck and finish smaller than the body.
EXTRUSION	Materials are melted in a screw-feeding cylinder and exit under the resulting pressure through a die of the profile corresponding to the package or precursor desired.
EXTRUSION BLOW MOLDING	Tubular extrusions (parison) are caught between two dies, which form the desired container shape, and are expanded with internal gas pressure.
THERMOFORMING	Sheets or films of monolayered or multilayered plastics and composites are heated and drawn, or forced under pressure of air or matching dies, into dies of the package shape desired.
COATING	One or more coatings of fluids or solids are consolidated by drying or compressing on substrates which may comprise plastics, foils, or fiber-based materials such as paper and paperboard.
LAMINATING	Two films or sheets are combined by applying between them and adhesive. Bonding results from drying, or heating and drying the included layer. Pressures may be applied to facilitate bonding.
CO-INJECTION MOLDING	Two or more layers of plastics are injected as in injection molding.
CO-EXTRUSION	Two or more layer are combined as they are extruded.
CASTING EXTRUSION	Molten plastic is deposit between two highly polished rotating rolls, which squeeze the material down to a flat film.

[1]Brown, Plastics in Food Packaging. np.

ATTRIBUTES OF PLASTICS USED IN FOOD PACKAGING[2]

PLASTICS	ADVANTAGES	DISADVANTAGES	FOOD USES
AMORPHOUS POLYAMIDES	Gas barrier improves with increasing humidity	Properties depend on moisture content	Films Blownware (as blends)
CPET	Resists heat to 200-225 C/ Very strong/ Barrier similar to PET	Tendency toward brittleness	Dual Oven ware
EVA	Tough/ Adheres to many substrates	Low stiffness/ Low barrier	Films Adhesives layers in multilayers
EVOH	Very high gas barrier if dry/ Stiff, strong/ Clear transparent films	Moisture sensitive barrier requires protection/ Forms gels in extrusion	Retortable barrier
IONOMER	Strong, tough, sealant/ Seals through particles/ Abrasion, grease and oil resistant	Limited service temperature	Films Sealant layers
NITRILE RESINS	Stiff, strong; monolayers bottle material/ High barrier to gases, oils/ High chemical resistance	Cannot use in contact with food above 150F	Backer boards for bacon/ Non-beverage liquids
PET	Gas barrier/ Can be blown into bottles/ clear transparent	Cannot be extrusion blow molded	Juices, hot-filled
PETG	Crystal clear transparency/ Can be extrusion blow molded	Low barrier to gases and moisture/ Limited heat deformation resistance in use	Spice Containers
POLYAMIDES	Good gas barrier if dry/ Good flavor and aroma barrier/Bonds directly to EVOH/Alloys with other polymers	Properties depend on moisture content	Cook-in bags Lamina in multilayers
POLYBUTYLENE	High resistance to heat/ Hot fill tolerant	Low stiffness	Coatings, adhesives/ PP Modifier
POLYCARBONATES	Tough, strong/ Retains stiffness at high temperature/ Clear	Low barrier to gases, moisture	Returnable bottles Water Jugs Structural layers in multilayers
POLYETHYLENE	Moisture barrier/ Flexible, tough/ Heat-seal adhesive	Absorbs some food flavor and aroma/ Hazy in thick sections	Blown bottles/ Film wrap Overlids
POLYMETHYL PENTENE	High heat resistance; retortable/ High clarity & transparency/ Release surface	Low modulus/ Low barrier to gases	Microwave oven ware
POLYPROPYLENE	Tough; clear transparent as random copolymer/ Tolerates retorting/ Orientation improves strength	Lowered stiffness at elevated temperatures/ Hazy in thick sections	Films Blown bottles Tubs for entrees
POLYSTYRENE	Stiff; Clear transparent/ Easily molded, thermoformed/ Moisture resistant	Low gas barrier/ Attacked by greases and oils	Dairy tubs Foam sheet-meat and produce trays
PVC	Tough, flexible, clear transparent/ Easily blown into bottle	Limited hot fill capability	Films Bottles for oils, dressings/

[2]Brown, Plastics in Food Packaging. np.

	forms/		Labels
PVdC	Oil resistant; moderate barrier		
STYRENE-BUTADIENE	High gas and moisture barrier/ Unaffected by moisture	Subject to thermal degradation during extrusion	Retortable barrier/ Cheese, processed meat wrap/
	Clear transparent/ Tough	Low resistance to heat/ Low barrier to gases	Barrier coating Films Bottles, esp. water

PRINCIPAL TYPE OF PLASTICS USED IN THE FOOD INDUSTRY[3]

- Polyolefins
  - Polyethylene (PE)
    - Low Density (LDPE)
    - Medium Density (MDPE)
    - High Density (HDPE)
  - Ethylene Functional Copolymers
    - Vinyl Acetate (VA)
    - Acrylic Acid
    - Ethyl Acrylate
    - Methyl Acrylate
  - Ionomers
  - Polypropylene (PP)
- Styrenics
  - Styrene-Butadiene (SB)
- Vinyls
  - Polyvinyl Chloride (PVC)
- Polyesters
  - Polyethylene Terephtalate (PET)
  - Polycarbonates (PC)
- Polyamide Nylon
- Vinyldene Chloride Copolymer (PVdC)
- Ethylene Vinyl Alcohol (EVOH)
- Nitriles

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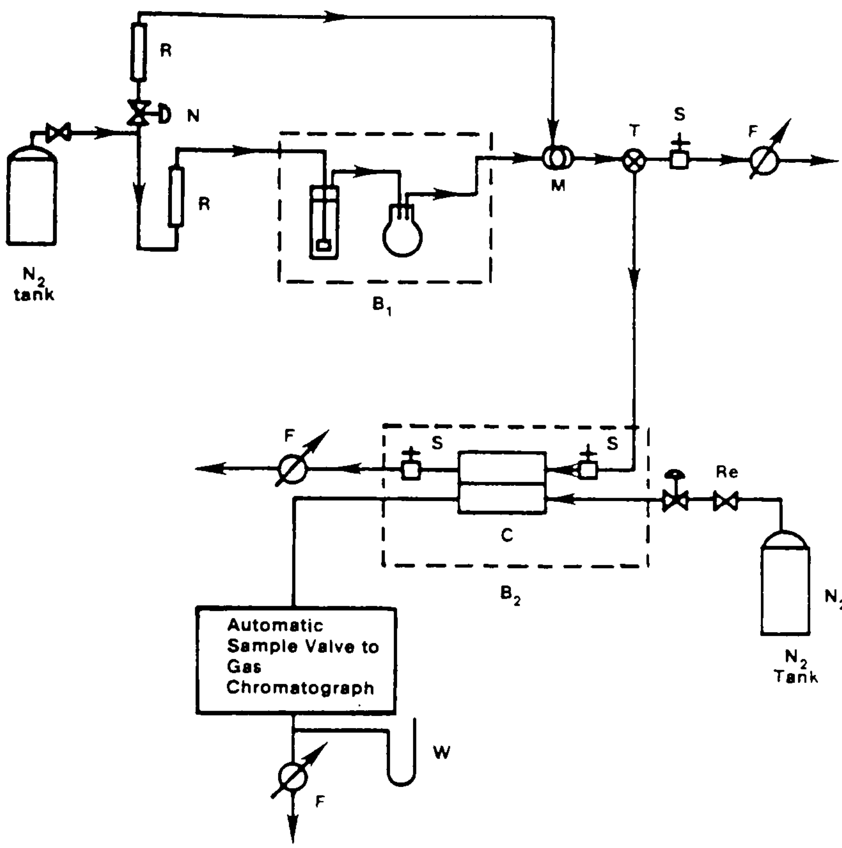
[3]Brown, <u>Plastics in Food Packaging</u>. np.

APPENDIX B

SCHEMATIC OF ISOSTATIC PERMEATION TEST APPARATUS



B_1 - Water bath, generation of permeant vapor phase diluted in Nitrogen
B_2 - Water bath (±0.1°C)
C - Cell
F - Gas flow bubble meter
M - Mixing device
N - Needle valve
R - Rotameter
Re - Regulator
S - Sample port
T - Three way valve
W - Water manometer

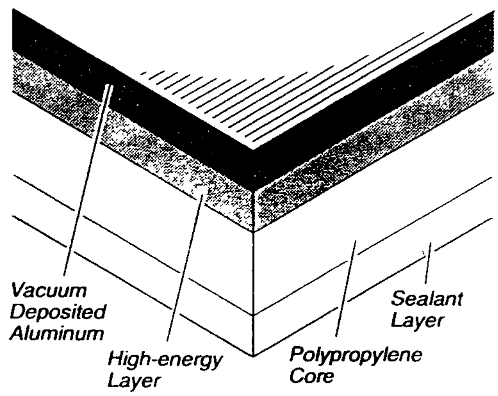
APPENDIX C

MATERIALS TECHNICAL SPECIFICATIONS

70 MET-HB

Description

BICOR MET-HB is a vacuum metallized, high barrier OPP film with a proprietary sealant layer. This film offers excellent oxygen and moisture barriers, hot tack, seal integrity, and lap seal range when used with a coextruded outer web. MET-HB is designed specially for adhesive and craze-free extrusion laminations.



Key Performance Characteristics

- ✔ Excellent oxygen and moisture barriers
- ✔ Low MST
- ✔ High adhesion of aluminum to film, offering 0% metal transfer
- ✔ Excellent hot tack

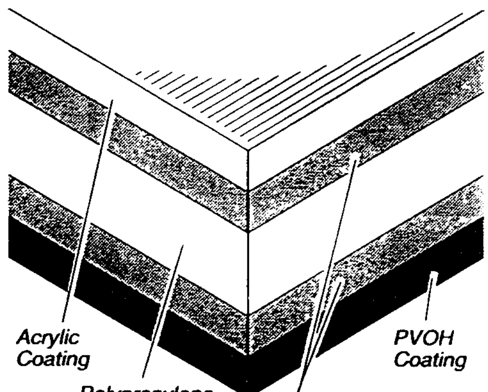
Property		Units	Mobil Test Proc. # NAF-OPP-4.10-QCT	70 MET-HB
Average Values of Critical Properties				
Yield		m^2/kg	-3-520	62.5
Optical Density			-3-474	2.3
WVTR, flat sheet* 38°C, 90% RH		$g/m^2/24$ hr	-3-518	.19
OTR, flat sheet* @ 23°C, 0% RH		$cm^3/m^2/24$ hr	-3-476	26
Descriptive Properties				
Gauge		microns	NOMINAL	18
Light Transmission		%	-3-456	1
Tensile Strength	MD	N/mm^2	-3-506	130
	TD	N/mm^2	-3-506	230
Dimensional Stability	MD	% change	-3-438	-4.5
@ 135°C	TD	% change	-3-438	-2.5
Crimp Seal Strength** @ 116°C, 1.4 bars, .75 sec		g/2.5 cm	-3-490	500
Crimp Seal Range** (lab) for minimum 200 g/2.5 cm seal strength		°C	-3-490	65

*Barrier specifications: WVTR – .31 maximum, OTR – 31 maximum
**Seal data is "descriptive" because this property is controlled during the film making process (MB-HB), but limited data suggests that the seal curve shifts about 5°C after metallization.

BICOR 84 AOH

Description

BICOR AOH is a two-side coated OPP film designed for high oxygen barrier applications and for use only as the outer web of a lamination. In lamination, this film is excellent for gas flush applications and is superior at maintaining initial gas concentration levels.



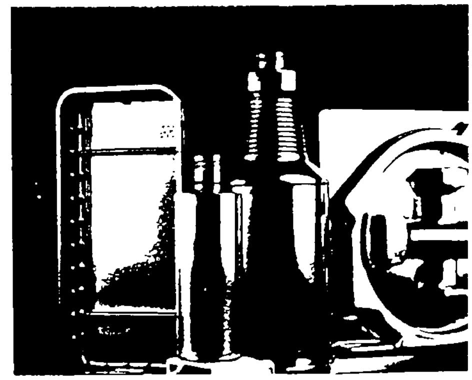
Key Performance Characteristics

- ✔ Excellent optical properties
- ✔ Breakthrough barrier performance
  - High oxygen barrier
  - Outstanding flavor and aroma barrier
- ✔ Receptive to water- or solvent-based printing (PVOH surface)
- ✔ Requires priming for extrusion laminations

Property		Units	Mobil Test Proc. # NAF-OPP-4.10-QCT	84 AOH
Average Values of Critical Properties				
Yield		m^2/kg	-3-520	49.7
Haze		%	-3-444	1.0
COF	acrylic/acrylic		-3-428	.21
OTR @ 23°C, 0% RH		$cm^3/m^2/24$ hr	-3-476	.62
Descriptive Properties				
Gauge		microns	NOMINAL	21
Tensile Strength	MD	N/mm^2	-3-510	140
	TD	N/mm^2	-3-510	230
Dimensional Stability	MD	% change	-3-438	-3.5
@ 135°C	TD	% change	-3-438	-3.0
WVTR @ 38°C, 90% RH		$g/m^2/24$ hr	-3-518	5.7
Gloss (45°)	acrylic		-3-442	97

Note: This product's oxygen barrier is at the limit of detection capability with current measurement equipment, so the variation is high relative to the average value. We guarantee, however, conformance to the specification maximum tolerance of 1.5 $cm^3/m^2/24$ hr.

Barex·
barrier resins



Barex® 210 Extrusion Grade

Barex® 210 Extrusion Grade Resin is an impact modified acrylonitrile – methyl acrylate copolymer with good gas barrier and excellent chemical resistance properties. It can be used for producing high barrier packaging by film and sheet extrusion, thermoforming and extrusion blow molding.

Typical Physical Properties

The physical properties of **Barex®** 210 Extrusion Grade resin summarized in this brochure are typical, or average properties measured in accordance with standard test methods. The information is the best currently available, however, it is subject to change without notice as new information becomes available.

Barex® resins are approved for food contact applications. For additional information on **Barex®** 210 Extrusion Grade or any of the other **Barex®** resins (210 Injection, 218 High Impact), please contact BP Chemicals, Inc. at the address shown on the reverse side.

	ENGLISH		METRIC		ASTM
PROPERTY	Value	Units	Value	Units	Method
General					
Density	72	lb/ft³	1.15	g/cm³	D792
Bulk Density	42	lb/ft³	0.67	g/cm³	D1895
Yield	24,080	in²-mil/lb	34.8	m²-25µm/kg	
Melt Index [1]	3	g/10 min	3	g/10 min	D1238
Mold Shrinkage	$2\text{-}5 \times 10^{-3}$	in/in	$2\text{-}5 \times 10^{-3}$	cm/cm	D955
Gas Permeability					
Oxygen (73°F, 100% RH)	0.8	cm³-mil/100 in²-24 hrs-atm	0.3	cm³-mm/m²-24 hrs-bar	D3985
Nitrogen (73°F, 100% RH)	0.2	cm³-mil/100 in²-24 hrs-atm	0.08	cm³-mm/m²-24 hrs-bar	D3985
Carbon Dioxide (73°F, 100% RH)	1.2	cm³-mil/100 in²-24 hrs-atm	0.45	cm³-mm/m²-24 hrs-bar	D3985
Water Vapor (100°F, 90% RH)	5.0	g-mil/100 in²-24 hrs-atm	2.0	g-mm/m²-24 hrs-atm	F1249-90

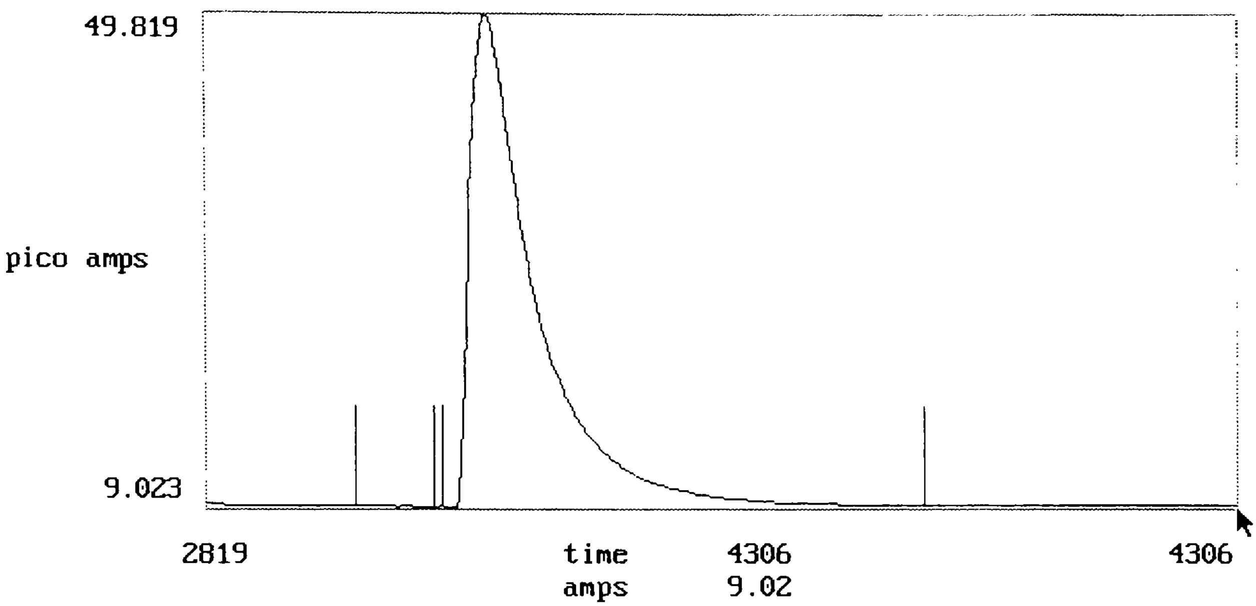
BP CHEMICALS

APPENDIX D

CALIBRATION CURVE

CALIBRATION CURVE

MATERIAL	Bicor[R] 70	PERMEANT	Pyridine
CALIPER	0.9 mil	CONCENTRATION	99.9%
BASELINE	9.12	VAPOR PRESSURE	16
INTEGRATION	4422.77	INJECTION	0.025
ugms	1.73		



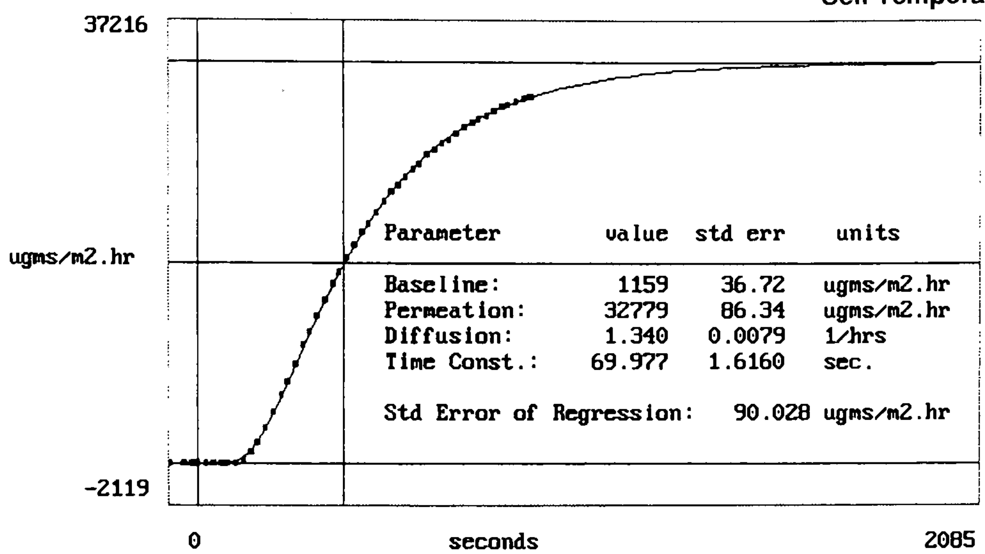
APPENDIX E

PERMEATION RATE CURVES

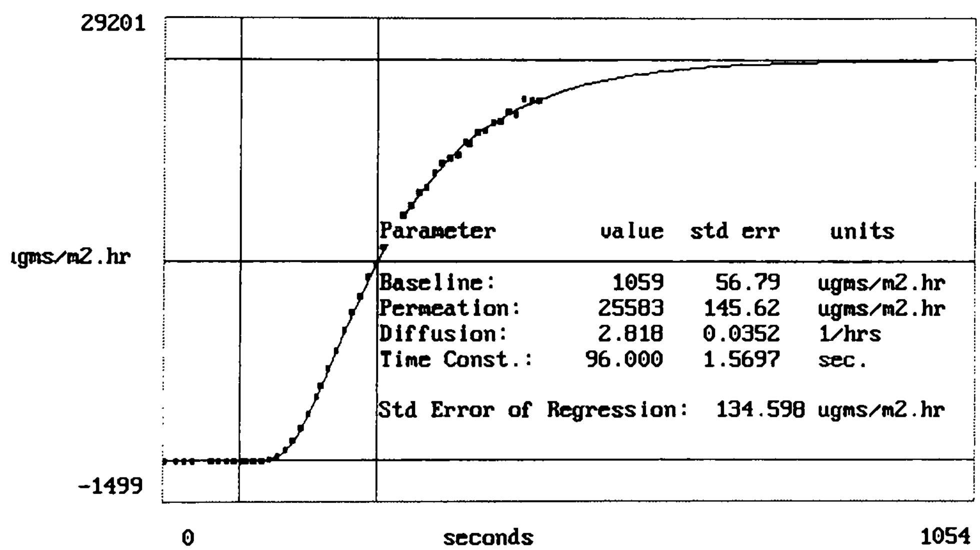
PERMEATION CURVES

Material Bicor[R] 70 MET-HB Permeant : Pyridine
FID Temperature 150°

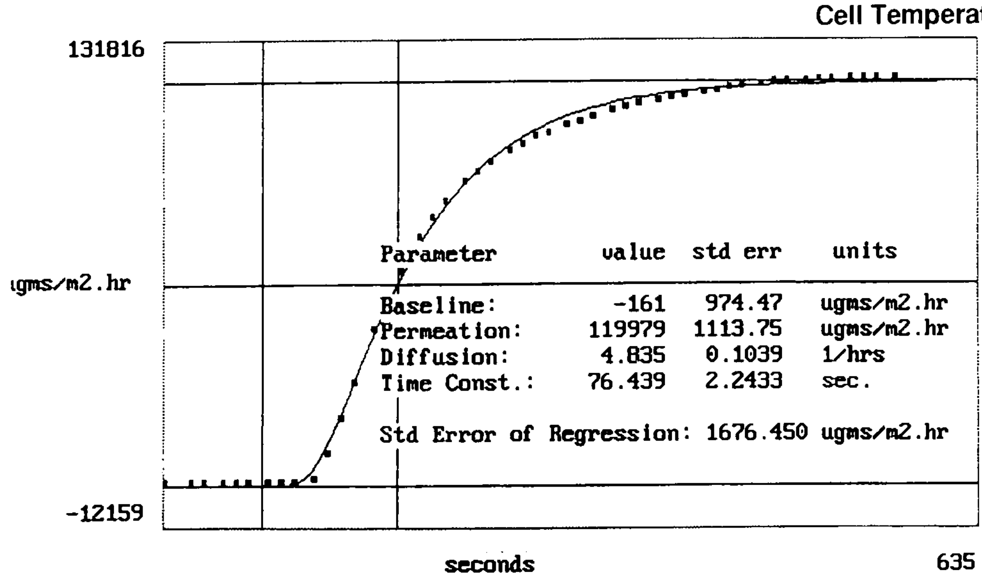
Cell Temperature 50°



Cell Temperature 60°



Cell Temperature 100°

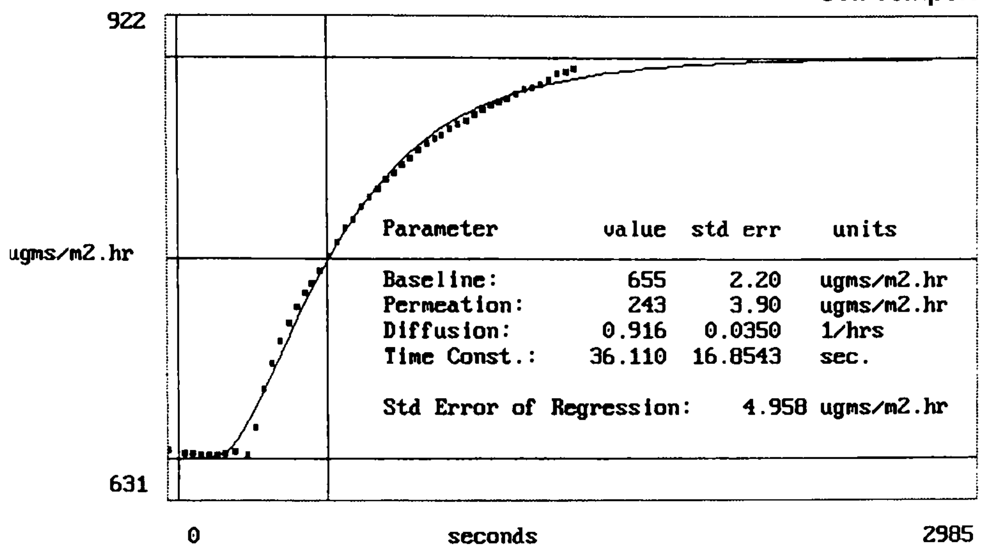


PERMEATION CURVES

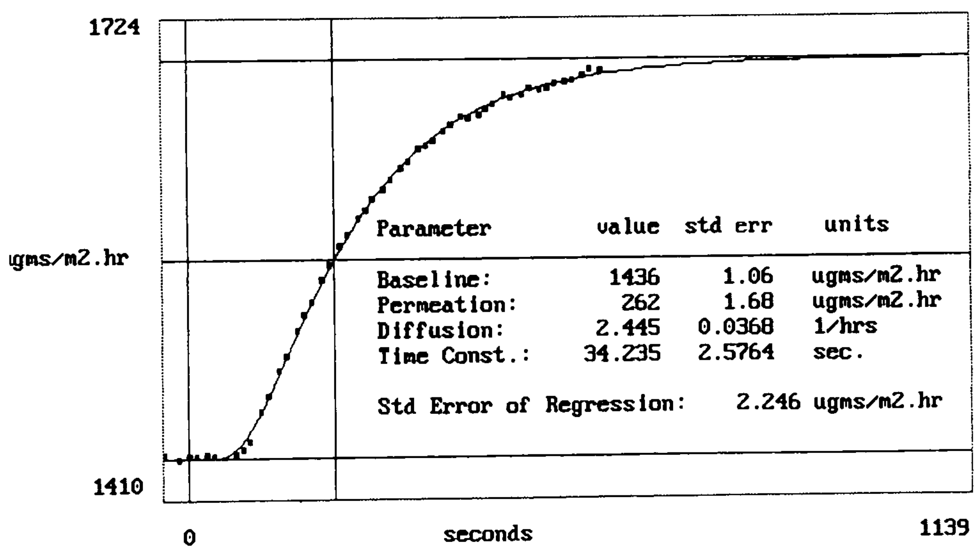
Material Bicor^{R} 84 AOH Permeant : Pyridine

FID Temperature 150°

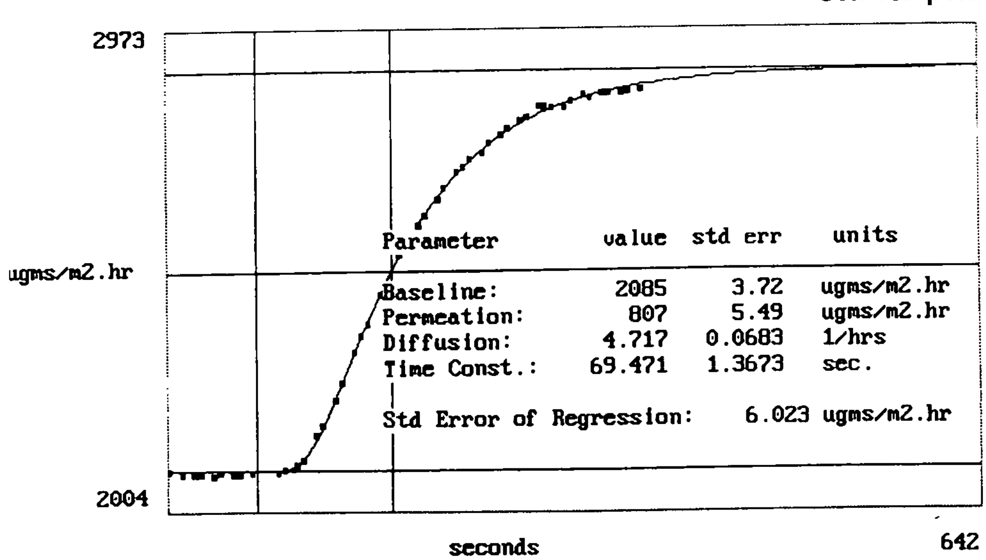
Cell Temperature 80°



Cell Temperature 90°



Cell Temperature 100°

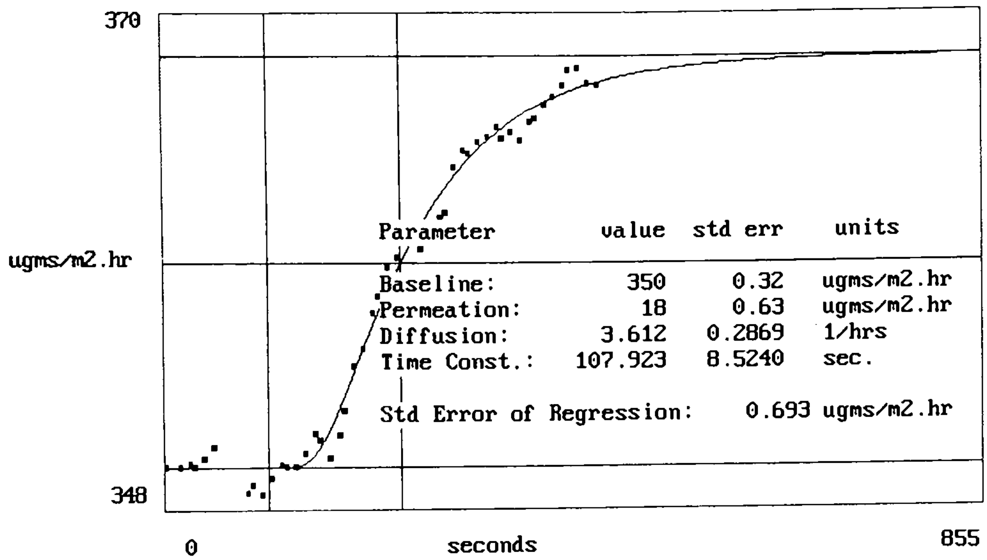


PERMEATION CURVES

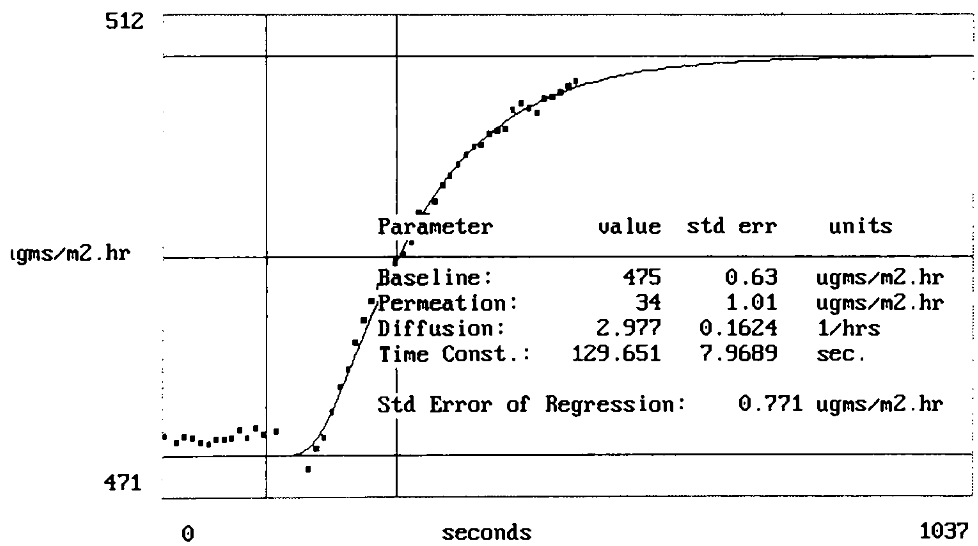
Material Barex[R] 210 Permeant : Pyridine

FID Temperature 150°

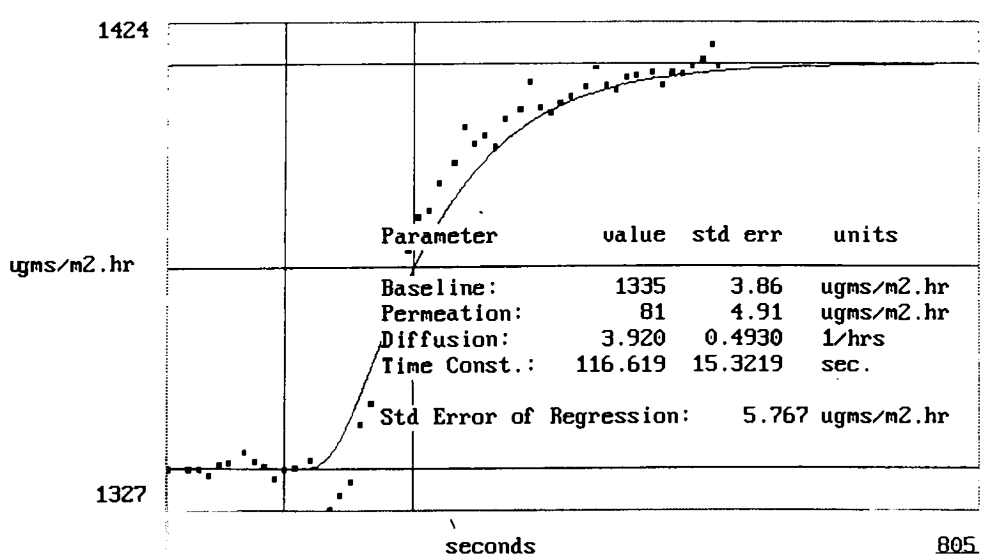
Cell Temperature 60°



Cell Temperature 80°



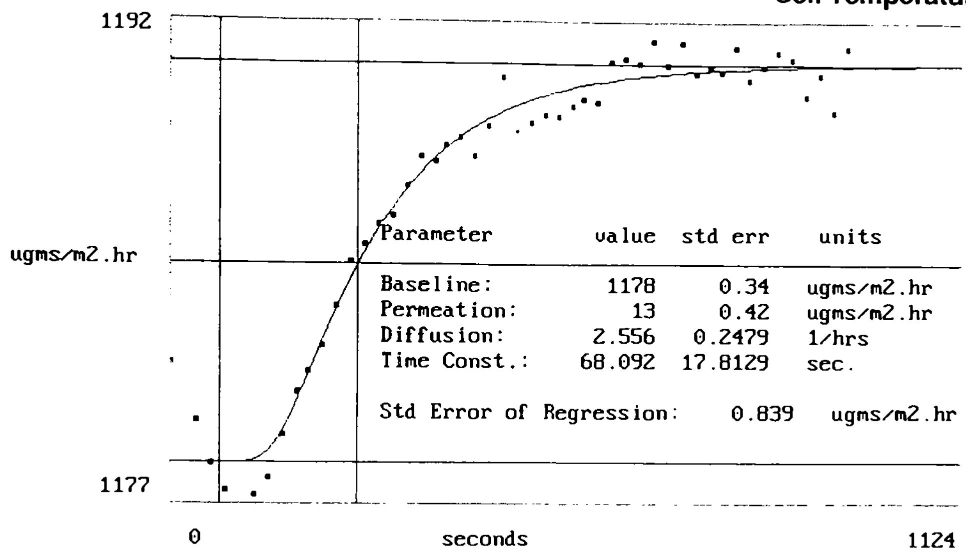
Cell Temperature 100°



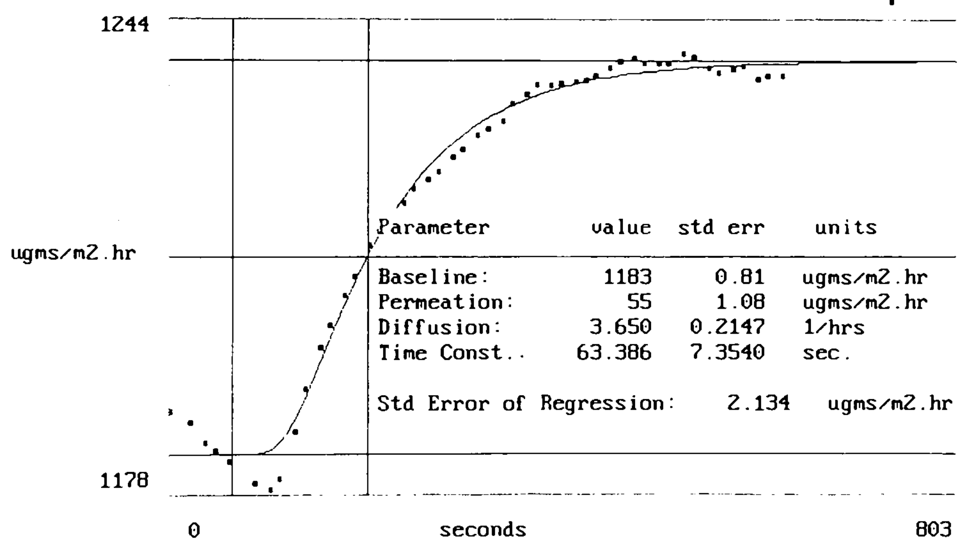
PERMEATION CURVES

Material Bicor[R] 70 MET-HB **Permeant :** Coffee
FID Temperature 150°

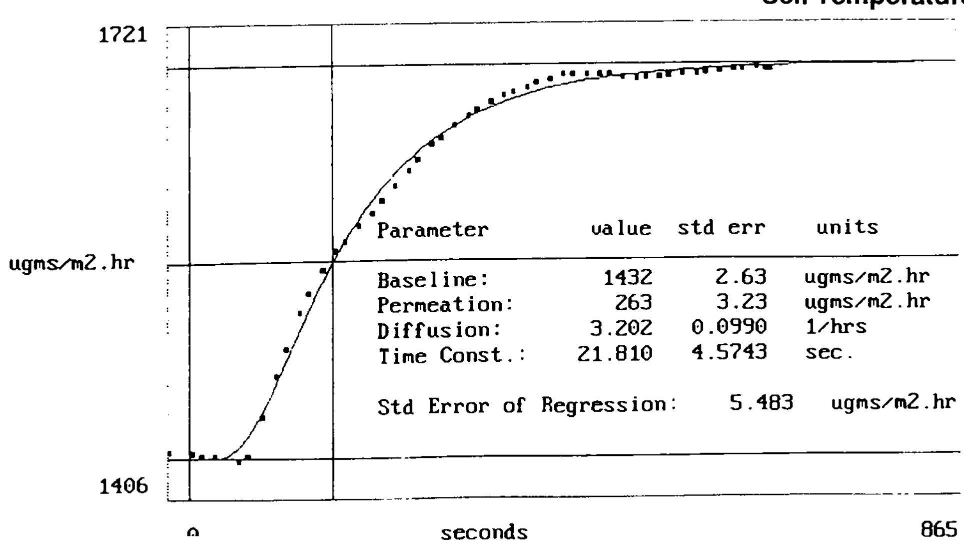
Cell Temperature 50°



Cell Temperature 80°



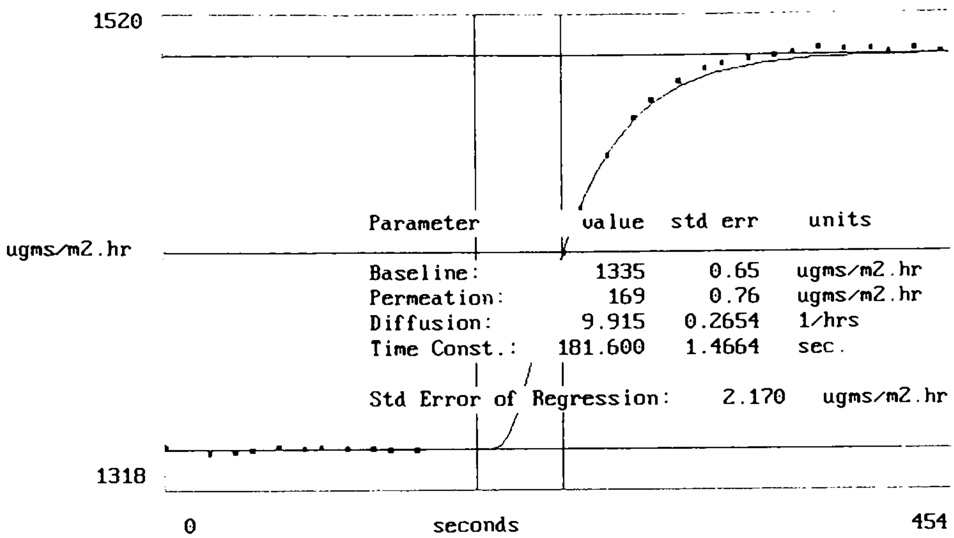
Cell Temperature 100°



PERMEATION CURVES

Material	Bicor[R] 84 AOH	Permeant :	Coffee
FID Temperature	150°		

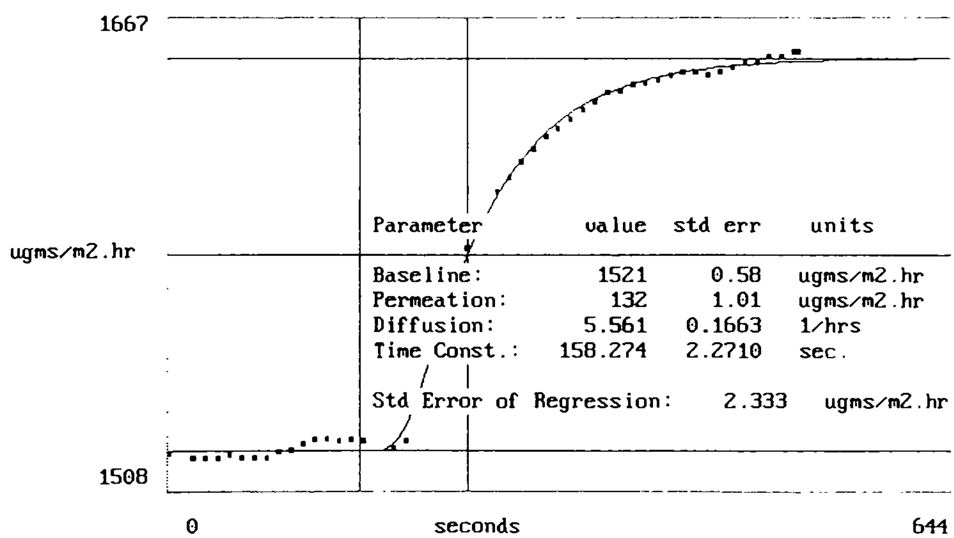
Cell Temperature 100°



Parameter	value	std err	units
Baseline:	1335	0.65	ugms/m2.hr
Permeation:	169	0.76	ugms/m2.hr
Diffusion:	9.915	0.2654	1/hrs
Time Const.:	181.600	1.4664	sec.

Std Error of Regression: 2.170 ugms/m2.hr

Cell Temperature 110°



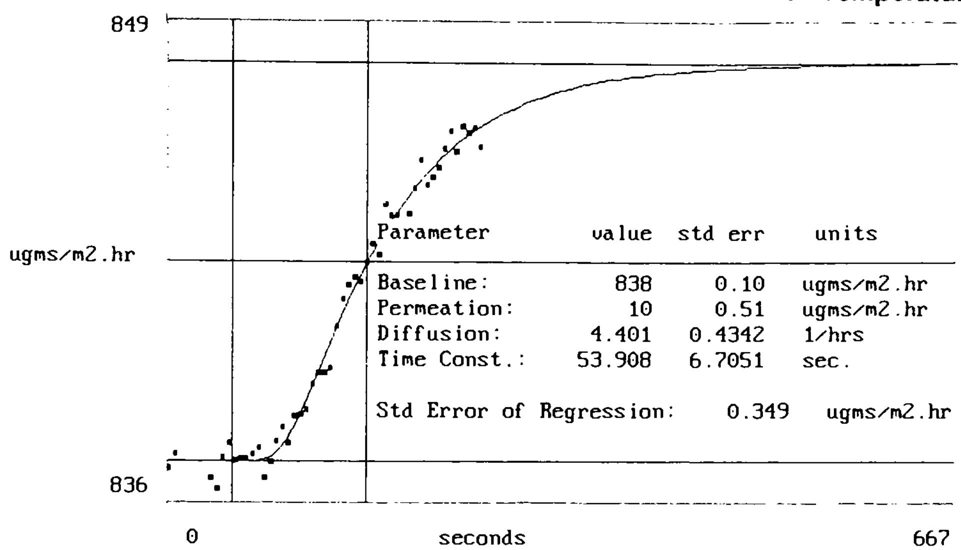
Parameter	value	std err	units
Baseline:	1521	0.58	ugms/m2.hr
Permeation:	132	1.01	ugms/m2.hr
Diffusion:	5.561	0.1663	1/hrs
Time Const.:	158.274	2.2710	sec.

Std Error of Regression: 2.333 ugms/m2.hr

PERMEATION CURVES

Material Barex® 210 **Permeant :** Coffee
FID Temperature 150°

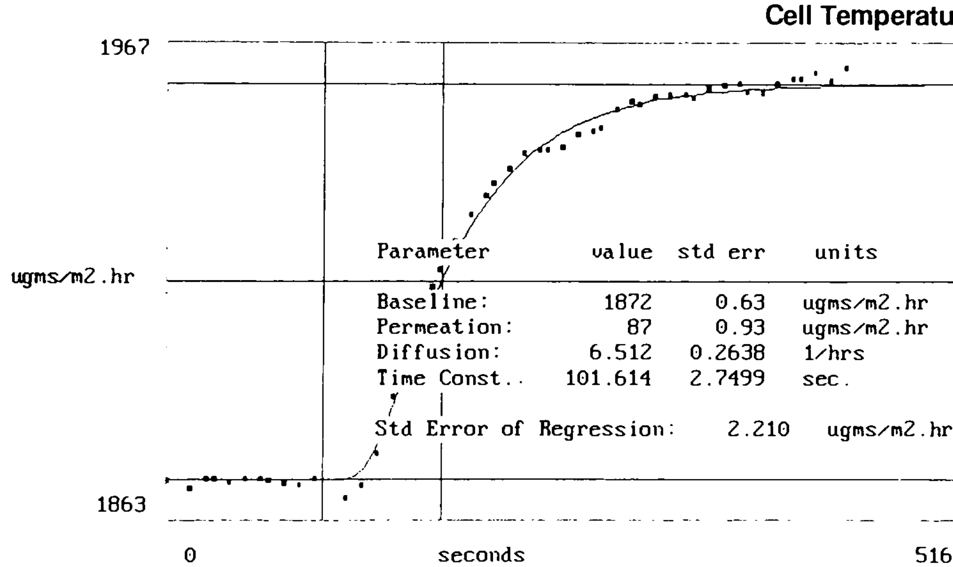
Cell Temperature 60°



Parameter	value	std err	units
Baseline:	838	0.10	ugms/m2.hr
Permeation:	10	0.51	ugms/m2.hr
Diffusion:	4.401	0.4342	1/hrs
Time Const.:	53.908	6.7051	sec.

Std Error of Regression: 0.349 ugms/m2.hr

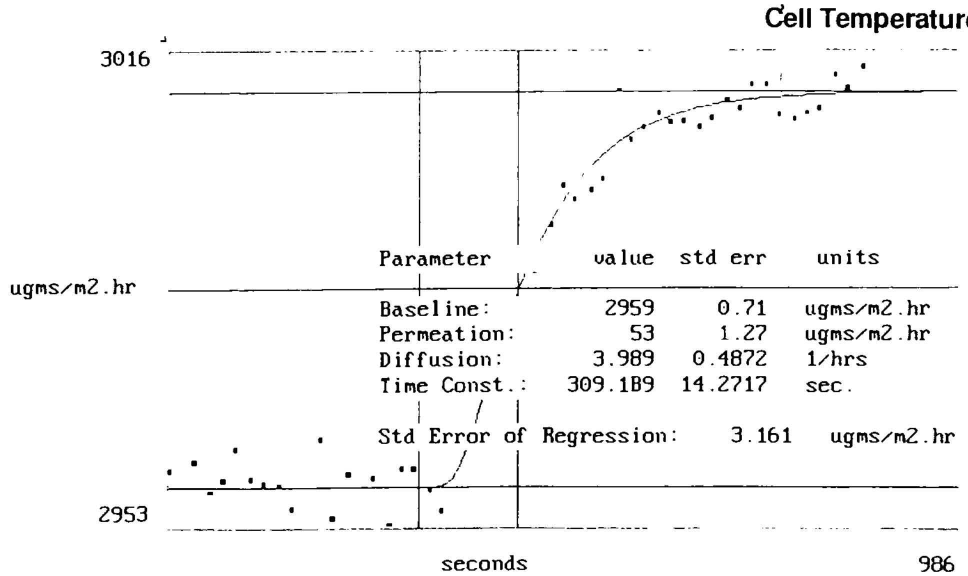
Cell Temperature 100°



Parameter	value	std err	units
Baseline:	1872	0.63	ugms/m2.hr
Permeation:	87	0.93	ugms/m2.hr
Diffusion:	6.512	0.2638	1/hrs
Time Const..	101.614	2.7499	sec.

Std Error of Regression: 2.210 ugms/m2.hr

Cell Temperature 110°



Parameter	value	std err	units
Baseline:	2959	0.71	ugms/m2.hr
Permeation:	53	1.27	ugms/m2.hr
Diffusion:	3.989	0.4872	1/hrs
Time Const.:	309.189	14.2717	sec.

Std Error of Regression: 3.161 ugms/m2.hr