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PRO-ACTIVE PACKAGING SYSTEMS FOR THE SELECTIVE SORPTION OF ORGANIC VOLATILES

By

Kuo-Chung Yin

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Abstract

Pro-active Packaging Systems for the Selective Sorption of Organic Volatiles

by

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Sorption studies showed that silica gel, aluminum oxide, Florisil, and Tenax-TA were effective sorbents for hexanal, ethyl acetate, and limonene, while Amberlite XAD-4 and XAD-7 showed varying levels of effectiveness depending upon the specific sorbate. Florisil dispersed within the adhesive matrix was found to be effective for the sorption of limonene, while the other adhesive matrix dispersed sorbent systems were ineffective. For the studies involving the adhesive matrix dispersed absorbent system, the sorbent loading level was 1.3 mg/cm^2.

The permeability of limonene through a polypropylene based laminate structure to which Florisil had been incorporated into the adhesive layer, showed that the Florisil was ineffective in modifying the transmission rate of limonene at the loading level 0.12 mg/cm^2 achieved.

TO MY PARENTS

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INTRODUCTION

In general, packaging passively protects food products but does not actively respond to changes in storage environment or to changes in the product itself.

The composition of the gas mixture within a food package can greatly influence both the quality and shelf life of the packaged product. For example, in certain cases it is desirable that a particular gas such as oxygen be totally removed. In other situations, it is important that the oxygen level be controlled at some particular concentration, below which it should not fall. Further, specific ratios of the concentration of oxygen to that of carbon dioxide may be required for extending the shelf life of a packaged product.

The control of gas composition within a package system has typically been approached by judicious selection of films with appropriate permeability characteristics. In this case, the packaging films are passive barriers whose properties are little altered with change in condition. However, conditions of humidity, temperature and the behavior of the packaged product do change. The result is that the internal environment of the package system can change with potentially disastrous results. The problem is particularly acute when the packaged product is metabolically active, or when there is a chemical change in the food.

For example, off-flavor and odor in a packaged product can develop during storage as a result of lipid oxidation. Volatile aldehydes (i.e., hexanal and pentanal) and other break down products of lipid oxidation, most likely give rise to the development of off-odor and flavor and the concomitant loss in product quality and acceptability.

Polymeric films are therefore needed which are pro-active and can react to metabolic or chemical changes associated with the product, allowing maintenance of the optimum internal package environment. The present study was designed to develop and evaluate pro-active polymer membranes which would interact with volatile organic compounds present within the package headspace or to reduce the rate of ingression of organic compounds from the external environment. To meet this objective, an active organic vapor sorbent will be incorporated into the adhesive layer of a polypropylene based laminated structure.
The structure proposed is:

Oriented polypropylene / sorbent impregnated adhesive layer / Saran-F Resin

The specific objectives of the study include:

- Determine the sorptive capacity of selected sorbents to volatile organic vapors

- Preparation and evaluation of the sorptive capacity of adhesive matrix
- Preparation and evaluation of the sorptive capacity of adhesive matrix dispersed sorbent
- Preparation of the oriented polypropylene / sorbent impregnated adhesive layer / Saran membrane
- Determine the barrier characteristics of the sorbent impregnated membrane structure

The preferred sorbent will be based on the results of studies designed to evaluate the sorption capacity and permeation characteristics of adhesive matrix dispersed sorbants.

LITERATURE REVIEW

1. Pro-active Packaging

Modified atmospheric packaging (MAP) and controlled atmospheric packaging (CAP) procedures have been known for decades, but they never quite seemed to live up to expectations. During the early '80s, MAP & CAP were touted as technologies that would revolutionize packaging. In retrospect, those hopes seem excessive and overpromised. Now expectations are more grounded in reality. Food packagers are realizing that in most cases, MAP or CAP can extend the shelf life of fresh food for only a few days (Demetrakakes, 1993).

A pro-active packaging system, when coupled with controlled atmospheric packaging or modified atmospheric packaging is a developing technology to meet new consumer demands. Basically, this technology includes an interaction between the package system itself and the packaged food. There are several basic techniques that have the potential of being combined in a packaging film surface to achieve shelf-life extension, and improve the nutritional quality of high moisture fresh food. These include:

1.1. Microwave Susceptor Packaging

One of the earliest applications of active packaging was microwave susceptors. It is known that the principle of microwave heating is to use the vibration of the water molecules among the food molecules to produce heat. In microwave heating, temperatures above 100°C may result as moisture evaporates in localized areas. However, if product crisping or browning is desired, product temperatures must reach to 200°C (Kwo, 1991). The designed susceptor material can convert incident energy into heat or focus heat in a predetermined region of the food to increase the heat's intensity.

Susceptor materials are used to achieve browning and crisping of foods such as pizza, fish sticks, French bread, popcorn and other foods. Usually the microwave susceptor material consists of a polymer film (Polyethylene terephthalate, PET) which has been metallized on one side, and laminated to paper or paperboard. The metal is usually aluminum, which is vacuum metallized to the substrate (Andrew, 1989). The polyester (PET) provides a heat resistant substrate and is placed in contact with the food products. Furthermore, the PET film can protect the aluminum coating from physical or chemical damage, and, it also prevents the aluminum coating from becoming an indirect food additive. (Perry, 1987) The paperboard provides mechanical support for the susceptor.

Design of a susceptor structure as a cooking aid to help brown and crisp a product, can achieve the high temperatures required for those specific needs.

1.2. Oxygen Scavengers

Eliminating food package oxygen has several major functions which include: (i)decreasing respiration rate; (ii)eliminating oxidation of polyunsaturated fats and oils, vitamins and pigments; (iii)preventing molds and aerobic bacteria growth; and (iv)controlling enzymatic browning. All of these can retard or inhibit the deterioration of food products or quality.

The Japanese pioneered the sachet category of active packaging, and it is now viewed as an integral tool in total-package development (Sacharow, 1991).

The Sachet, also called smart films and freshness enhancers, are added to the package or film. The most well-known oxygen scavengers take the form of a small sachet containing various metallic reducing agents, including:

(1). Powered iron oxide
(2). Ferrous carbonate
(3). Ferrous compounds
(4). Metallic platinum

These systems, which often react with water from the food to produce a reactive metallic reducing agent, are combined with an assortment of catalysts (Anonymous, 1990). The system manufactured by the Mitsubishi Co. under the trade name

"Ageless" is the primary oxygen scavenger now used by the food industry worldwide and can provide a level of 0.01% oxygen over a period of three months(Toyama *et al.*, 1980).

Non-metallic formulations also have been developed to ease problems associated with product oxidation. These systems employ compounds such as ascorbic acid (Vitamin C) and its associated salts. Recently Zenner and Salame (1989) described a new type of oxygen scavenger system, called "Longlife", which is comprised of an organo-metallic molecule that has a natural affinity for oxygen. This compound functions in a similar fashion to hemoglobin, which transports oxygen in animals. Oxygen molecules are irreversibly bound by hemo-like molecules, and, thereby, free oxygen is extracted from the surrounding environment. A number of these complexes have been immobilized on insoluble supports in functional form with the "Longlife" system.

Another recent development in active packaging materials is the "Oxbar" system, which is comprised of PET as the main component (96%), MXD-6 Nylon as the oxidizable component (4%) and an organic cobalt salt added as the oxidizing catalyst, at a 50-200 ppm level. This composition can be extruded to make bottles, which are said to be able to maintain the oxygen level inside the container as low as zero for two years (Yoshii, 1992).

Linking the oxygen-binding molecules onto inorganic substrates produces an insoluble oxygen sorbing system, which can be used effectively within liquid or semi-liquid products.

Another method to control the oxygen in a food package in an active way rather than a passive way (i.e., permeation only) would be by the use of an enzyme (i.e., glucose oxidase and alcohol oxidase) immobilized within a membrane, which would react with some substrate to scavenge incoming oxygen.

It is important to note that an oxygen-free atmosphere can be conductive to the growth of many anaerobic microorganisms such as *Clostridium botulinum*. Therefore, when applying oxygen scavengers to food products, there are several criteria which should be taken into account to include:

- water activity-below 0.92
- pH value-lower than 4.7 or higher than 9.1
- distribution temperature-below 3°C

(Yoshiaki, 1990)

Oxygen has been shown to have significant detrimental effects on food. Decreasing food package oxygen levels can help maintain product quality, flavor, taste, appearance and nutritional value.

1.3. Retorted EVOH Multilayer Structure with Excellent Oxygen Barrier Properties

Ethylene vinyl alcohol copolymers (EVOH) are excellent oxygen barriers when used under dry conditions. However, an inherent problem associated with EVOH copolymers is their high moisture sensitivity. Consequently, oxygen permeability increases by a factor of one hundred when containers containing an EVOH barrier layer are subjected to retort conditions, which involve exposing containers to steam or pressurized water at temperatures of 96 to 135°C. Recently, Tsai and Wachtel (1985) developed a multilayer plastic food container made with an EVOH oxygen barrier layer, which could be packed on commercial filling, can-closing, and thermal-processing equipment. The structure of the multilayer container is as following:

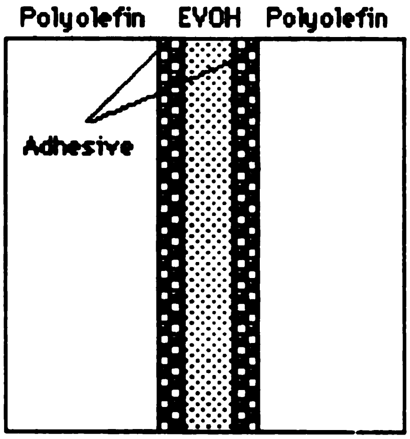


Figure 1. Schematic Diagram of the Multilayer Structure

The incorporation of a desiccant into the adhesive layers, however, overcomes the short term permeability increase of a retorted container due to moisture plasticization and also greatly reduces the permanent increase due to retort path dependence (Tsai *et al.*, 1985).

1.4. Ceramic-filled Polymeric Films for Packaging Fresh Produce

From sachet theory, quality problems associated with the food product itself can be solved. However, on the other hand, potential problems involving consumers arise with the use of Sachet technology. The small sachet labeled " Do not eat." can have potential toxicity, if the sachet were accidentally consumed. For example, the LD_{50} (lethal dose that kills 50% of a test population) for iron is 16g/Kg body weight. The largest sachet commercially available contains 7 grams of iron so this would amount to 0.1g/Kg for a 70 Kg person, or 160 times less than the lethal dose. There is, therefore, concern over the toxicity of a Sachet pouch in the food package, which suggests the need to develop a more friendly pro-active package for food products (Labuza *et al.*, 1989)

Lee *et al.*(1992) described a new pro-active packaging material which consisted of a ceramic-filled polymeric film, which was being marketed in Japan and Korea for packaging or storing foods, especially for fresh produce. It has been well established that the storage quality of fresh produce can be extended by MAP, usually with reduced oxygen and elevated carbon dioxide levels. The optimum gas composition of the modified atmosphere can be attained and maintained by selecting appropriate values for the package parameters (permeability, thickness, surface area) to match the respiration rate of the produce.

The respiration rate of fresh produce depends on the oxygen, carbon dioxide, and ethylene concentrations inside the package. A climacteric fruit or vegetable ripens as the levels of certain internal hormones build up in the tissues. A key hormone is the hydrocarbon gas ethylene that, even in a small amount, can greatly accelerate the respiration rate of packaged fresh produce. Thus, absorbing or allowing ethylene to permeate from the package can reduce the respiration rate and extend the storage quality of the produce.

Ceramic filled polyethylene film exhibit higher CO_2 to O_2 permeability ratios (3.6-5.0 versus 3.3-3.5) and also higher ethylene to O_2 permeability ratios(1.5-1.8 to 1.1-1.5) than those of low density polyethylene (LDPE) film, which is the most common package film for fresh produce. This is especially true at lower temperatures. These permeability ratios are particularly important in modeling the MAP of fresh produce. The reason is that the ceramic filled films have higher activation energies for O_2 permeability and slightly lower activation energies for CO_2 and ethylene permeability when compare to LDPE. The O_2 permeation rates for ceramic filled films were therefore more sensitive to temperature change, while the permeability of CO_2 and ethylene through the ceramic-filled films were less susceptible to temperature, when compared to the non-ceramic filled structure. Activation energy is also a significant influence on the design of MAP for food packaging (Lee *et al.*, 1992).

1.5. Absorbent Pad for Meat and Poultry Food Products

Rhodes *et al.*(1991) pointed out that meat and poultry food products are typically sold in a supporting tray that is overwrapped by a transparent plastic film or in transparent plastic bags, which enable the consumers to view and inspect the food products. The public has become accustomed to purchasing meat and poultry food products within such packages, not only because the products can be easily viewed and inspected, but also because consumers believe that the food products contained within such packages are maintained in a sterile environment. In fact, it is true that supporting trays with transparent plastic overwrap or transparent plastic bag do protect the food products from external contamination, but consumers are not always aware of the potential for internal contamination which is the result of juices or liquids excuded from such food products. It has been found that juices or liquids excuded from such food products can support the rapid growth of bacteria which migrate back into and around the food product, resulting in spoilage or deterioration of product. Furthermore, such excuded liquids or juices create an undesirable visual impression to a consumer, giving the consumer the impression that the food products are unappealing.

Some of the prior designs have suggested a variety of additives, which can be incorporated into the absorbent pad to increase the sorption capacity of the absorbent pad. However, none of the proposed additives have functioned well enough to absorb and retain the excuded liquids or juices within the absorbent pad. Rhodes *et al.*(1991) have described a new and improved absorbent pad incorporating superabsorbent granules therein, and a method for constructing the same. This objective is achieved by including the superabsorbent particles in a network formed between cellulosic fibers and thermoplastic fibers (or other similar fibers), which are bonded in a thermobonding process. Thus, the superabsorbent particles, which are homogeneously dispersed throughout the absorbent layer , when absorbing liquid, are prevented from moving within the material. It is believed that this property is sufficient to prevent reverse migration of the juices back to the meat product, even when the upper sheet is perforated. In applications where higher demands are placed on the absorbent pad, it may be constructed with an imperforated upper sheet, but the sides thereof may still be unsealed so that the juices are absorbed through said sides.

1.6. Miscellaneous Pro-active Packaging Systems

An approach to extend shelf life, by preventing mold generation on food, staling or surface hardening of baked food and insect growth, has been to spray ethanol or another alcohol on the surface of the food product (Yoshiaki, 1990)

A recent active package system based on this concept involves an ethanol emitter consisting of a pouched, powdered alcohol-discharging agent which acts to time release ethanol vapor. The sachet contains microencapsulated, food-grade ethyl alcohol, containing 55% alcohol by weight. It allows the controlled release of the ethanol vapor within the container, where it deposits on the food surface (Sacharow, 1991).

Another active packaging concept involves the release of an active agent into the package atmosphere. This approach, used by the cereal industry for a number of years, incorporates antioxidants such as 3-tertiarybutyl-4-hydroxyanisol (BHA) or 3,5-ditertiarybutyl-4-hydroxytoluene (BHT) into a wax liner. The proposed mechanism of antioxidant activity involves the following 3 step process: (i) antioxidant diffusion through the polymer bulk phase; (ii) evaporation of antioxidant from the surface of the packaging material; and (iii) subsequent antioxidant sorption onto the surface of the packaged product, where it provides its protective action. Hoojjatt et al. (1987) have also reported on the kinetics of diffusion of BHT from polyethylene films and the influence on product stability. The result showed that at ambient temperature (23°C) approximately 80% of BHT diffused out of the package to the surrounding environment, while approximately 20% of the added BHT transferred into the cereal and provided enhanced protection to the cereal product.

A new approach being evaluated to extend the shelf life of refrigerated foods is to decrease the water activity (Aw) at the food surface. Showa Denko in Tokyo, Japan has developed and is presently marketing such a film (Pitchit Film) directly to the consumer. The film is a sandwich like structure composed of two sheets of polyvinyl alcohol (PVA), sealed along the edge, between which is a layer of propylene glycol. When fish or meat is wrapped in the sheet, excess water is released by osmotic pressure, resulting in microbial inhibition. (Labuza *et al.*,1989)

Another active packaging which has been developed, was designed to maintain the product at constant temperature. Because of the concern for rapid microbial growth with refrigerated foods as the temperature increases during refrigerated distribution and transportation from the store to the home, considerable care must be exercised with such foods. One approach to solving this problem would be to insulate the food, using a specially designed insulating packaging material. One commercially available material with potential for such an application is "Thinsulate®" from the 3M company, which is a special nonwoven plastic with considerable air pore space. Another approach is to increase the thermal mass of the package so as to absorb temperature abuse. The Adenko company of Japan has recently developed a new product called the "Cool Bowl". It is a double walled PET container in which a gel is deposited between the walls. The "Cool Bowl" is prechilled with the food, and thus acts as a portable cooler when the product is moved to a warmer temperature environment. (Labuza *et al.*, 1989)

An active polymeric film has recently been developed as an anti-bacteria film, where silver and zinc ions have been bonded to the surface of a synthetic microporous zeolite. The zeolite is composed of hydrous aluminum silicate. The metal ions generate active oxygen which is capable of stopping cell metabolism in most bacteria, including staphylococcus aureus, salmonella typhimurium, and escherichia coli. The active zeolite has been found to be effective at concentrations as low as 2 ppb (wt/wt). It is usually incorporated in a polymer that functions as an inner layer in a multilayer packaging film. Almost any polymer material can be used to contain the zeolite filter (Bigg, 1992).

Out of the most interesting active packaging or smart packaging systems is the Time-Temperature Integrators packaging. The quality of a refrigerated food product and its useful shelf life is very much dependent on its temperature history. From production, through transportation, storage and consumption, it is very difficult to control the environmental temperature to which the packaged product is exposed. Usually shelf life estimations are based on assumptions, which involve either (i) the most probable average temperature of the food; or (ii) a worst case temperature distribution. Each one of these two approaches has its own inaccuracy. For the first approach, if the shelf life was estimated from the most probable average temperature values, the food products may become unacceptable or a health hazard, before the stated end of shelf life because of temperature abuse above the average assumed temperature. If the second approach is applied, the assumption may be too conservative to estimate the product actual shelf life, since the package may never be exposed to adverse conditions. To solve these problems, a monitor can be placed on the package, which can record the product temperature history and thus estimate the remaining shelf life. Several types of monitor tags or Time-Temperature Indicators have been developed. Blixt and Tiru (1976) first suggested the use of this type of monitor for refrigerated foods. Linsay (1985) reported that such indicators are absolutely essential for CA stored ocean fish, because of the potential of pathogens. However, there is no general approach that would allow correlation of the response of the Time-Temperature Indicator to the quality changes of a food product of known deterioration modes, especially nutrient loss, without actual testing. It is hard for the food manufacturer to make a decision on whether to use and how to use a Time-Temperature Indicator. Furthermore, it is difficult to decide which Time-Temperature Indicator is the most appropriate type for a specific product. This is probably one of the reasons that there are limited commercial applications for Time-Temperature Indicators as active packaging devices.

2. Flavor Interactions with Packaging

The so-called high technology packaging systems such as retort and hot fill pouch, blow-molded, aseptic, low acid, modified atmosphere, chilled, and precooked food packages have a major responsibility for maintaining food product quality.

2.1. Off-flavors from Packaging

Packaging materials may contain components which migrate from the package into the package contents and adversely affect product flavor characteristics or are of concern for health reasons. With respect to human health considerations, the use of polyvinyl chloride food packaging was the subject of a number of studies in the late 1960's and early 1970's, with the discovery that vinyl chloride monomer (VCM) is a carcinogen. This concern continued in the late 1970's with the suspicion that acrylonitrile (AN) monomer was a carcinogen (Joseph, 1986).

Another concern is related to product contamination as a result of the migration of organic solvent residues from printing and coating processes. The use of volatile organic solvents in the printing industry is widespread, and while this issue has diminished due to a decline in rotogravure printing and the conversion to water-based inks, this problem has not disappeared entirely. Moreover, the adhesives and polymer resins have themselves been identified as the source of off odors in some cases. For instance, solvent-based adhesives and polyethylenes extruded at excessive temperatures are most often involved (Melissa, 1992).

Possible migrants from plastics include: residual monomer, low molecular weight polymers, catalyst residues, plasticizers, antioxidants, antistatic agents, lubricants and slip agents, antiblock agents, colorants, blowing agents, residual solvents, emulsifiers, defoamers, chain transfer agents, light stabilizers, fire retardant agents, polymerization inhibitors, reaction products, and decomposition products (Giacin et al. 1986)

2.2. Flavor and Aroma Migration

The transfer of flavors into and out of packages has been recognized for a number of years to be a problem associated with polymeric packaging materials. These mass transfer processes have variously been described as flavor scalping, sorption, or permeation, as well as by other terms such as partition equilibrium. For example, fruit flavors can be scalped from beverages and even permeate through polyethylene bottles because of the high solubility of flavor volatiles in polyethylene and its poor barrier characteristics to organic vapors. The phenomenon of flavor losses from food products to their package is a new one in concept and significance.

Aroma and flavor volatiles are comprised of numerous organic compounds, which have complex structures and varying size distributions. As a result of both structure and molecular size, constituents of flavor or aroma volatiles can dissolve and diffuse in polymeric packaging materials to different degrees. For those aroma or flavor compounds which dissolve and/or diffuse rapidly in plastic packaging, their loss in product concentration is readily experienced.

2.3. Selected Organic Sorbates

2.3.1. Off-flavor Produced by Lipid Oxidation

Lipids, especially those containing polyunsaturated fatty acid, are easy oxidized, and lipid oxidation in food products can result in the development of rancid flavors. Linoleic acid is a predominant unsaturated fatty acid in many food products, which can be oxidized to hexanal, octanal, and 2,4 decadienal (Fritsch et al., 1976). The formation of hexanal, caproic aldehyde, not only results in the development off-odors emanating from the food, but may also lead to further reactions with other food constituents, such as proteins, which will lower the nutritional quality of the food product (Karel, 1973). Consequently, the removal of hexanal via its selective sorption by the packaging material could result in extending the keeping quality of the packaged product.

2.3.2. Off-flavor Migrated from Packaging Materials

Migration of low molecular weight species like residual monomers, oligomers, solvents, catalysts, etc., from polymeric packaging materials is a subject of growing attention and concern in the packaging field in recent years (Miltz, 1986).

Ethyl acetate, acetic acid ethyl ester, is a common solvent used as the reaction medium for polymerization, printing, or adhesive coating and must be removed by drying after the completion of the printing or laminating processes. Residual solvent, such as ethyl acetate is susceptible to migrate from the package to the product. The migration of residual solvent such as ethyl acetate remaining in the packaging film can result in an undesirable odor existing in the interior environment of the package (Culter, 1992).

2.3.3. Product Flavor Sorption

Citrus flavors are among the most popular fruit flavors for beverages. D-Limonene, 1-methyl-4-(1-methylethenyl) cyclohexene, is one of the major volatile constituents which is responsible for orange flavor, as it is for grapefruit, lemon, and lime flavors.

Studies have shown that many aroma moieties can be readily absorbed into plastic packaging materials. Most investigations have been made concerning absorption of terpenes, occurring in orange juice, into packaging material (Nielsen *et al.*, 1992). Durr *et al.*(1981) reported that a distinct loss of d-limonene in orange juice stored in polyethylene-lined cartons occurred after the first two weeks of storage. Berens (1978) found that absorption of limonene by polyolefin structures caused swelling of the polymer matrix. The loss of d-limonene can be explained on the basis of the permeation or solubility phenomenon, also referred to as "scalping." D-Limonene may also serve as a carrier for the minor oil-soluble flavor constituents, known to be important to orange juice.

3. Sorbents

Recently, commercially available active polymeric films and containers have been introduced in a number of countries for packaging or storing foods. Out of the most successful examples of such active packaging is ceramic filled polyolefin film or sheet. The manufacturers claim that these materials emit far infrared radiation or absorb ethylene that can help to extend the shelf life of fresh produce (Lee *et al.* 1992).

3.1. Alumina Super Activity I

Alumina super activity I, which consists mostly of Al_2O_3, is useful for the chromatographic analysis of light hydrocarbons. Unsaturated hydrocarbons are retained longer than saturated ones. They are also used for the drying and "sweetening" of liquid or gas streams.

3.2. Synthetic Amorphous Silica Gel

Silica gel is based on $SiO_2 \cdot xH_2O$. Employed for preparative and classic column chromatography, synthetic amorphous silica gel is commonly used for fixed gases, such as hydrogen, air, carbon monooxide, methane, ethane, and light hydrocarbons. It is also useful for dehydration of gases and liquid. Hydrogen-bonding compounds are strongly sorbed by silica gel.

3.3. Florisil

Florisil is a highly selective magnesium silica gel sorbent which was developed for the clean-up of pesticides and other organic residues. Florisil is activated at 1250°F and is packaged in amber glass bottle.

3.4. Amberlite XAD-4

Amberlite XAD-4 is a polymeric sorbent supplied as insoluble white beads. It is a non-ionic, crosslinked polymer which derives its absorptive properties from its patented macroreticular structure (containing both a continuous pore phase), high surface area and the aromatic nature of its surface. This structure gives Amberlite XAD-4 polymeric sorbent good physical, chemical, and thermal stability. Amberlite XAD-4 polymeric sorbent can be used through repeated cycles, in column or batchwise modes, to sorb hydrophobic molecules from polar solvents or volatile organic compounds from vapor streams. Its characteristic pore size distribution makes Amberlite XAD-4 polymeric sorbent an excellent choice for the sorption of organic substances of relatively low molecular weight.

3.5. Amberlite XAD-7

Amberlite XAD-7 is an acrylic ester polymeric sorbent that differs from the Amberlite XAD-4 in that it has a somewhat more hydrophilic structure. Amberlite XAD-7 is a crosslinked polymer which is supplied in the form of hard insoluble beads. Amberlite XAD-7 can be used to sorb non-polar solutes from aqueous systems, and can also sorb certain polar solutes from non-polar solvent. In the absence of functional sites, the polymeric sorbent derives its sorptive properties from its combination of macroreticular porosity, pore size distribution, high surface area and the aliphatic nature of its structure. It also has good thermal stability and very good physical durability.

3.6. Tenax-TA

Tenax-TA is a porous polymer that is based on 2,6-diphenyl-p-phenylene oxide. It was developed by AKZO Research Laboratories and is marketed by Buchem B.V. of The Netherlands. Tenax-TA contains a low level of impurities and has been replaced by Tenax-GC. Tenax-TA can be used as both a column packing and as a trapping absorbent for organic volatile and semi-volatile compounds.

Tenax-TA is suitable for the separation of high boiling polar compounds such as alcohols, polyethylene glycol compounds, diols, phenols, mono and diamines, ethanolamines, amides, aldehydes and ketones.

4. Multilayer Laminations

Multilayer laminations are combinations of two or more films or other non-plastic materials into a single structure (Manypenny, 1988). The requirements for the protection of food products can not often be reached by the use of a single layer film. Therefore, it is necessary to have laminations, with each layer contributing to some particular aspect of package performance. A typical general purpose laminate, such as those used for the packaging of snack foods, meats, and cheeses, consists of an outer barrier layer laminated to an inner heat seal layer.

Sarans®, such as the Saran F-resin 310 used in present study, are high barrier polymers, which are characterized by: excellent water vapor barrier, good gas barrier, excellent oil and grease resistance, toughness, flexibility, and heat-sealability. Saran F-Resin 310 (supplied by Dow Chemical Company, Midland, MI 48867) is a solvent-soluble, non-crystalline copolymer of vinylidene chloride with other monomers. Lacquer solution of Saran F-Resin produce extremely dense, impervious films from dried coatings (Dow Chemical Company brochure).

The unique properties of Saran F-Resin 310 makes it especially valuable in a variety of coating applications. The majority of these coating applications are in flexible packaging. Saran F-Resin 310 has a higher molecular weight than do the other Saran F-Resins. As a result, coating of this resin are tougher, have more extensibility, and provide a somewhat higher heat-seal strength at elevated sealing temperatures, relative to the other Saran F-Resins.

5. Adhesives

5.1. Characteristics of Adhesive

The strength of any union between adhesive and adherend depends fundamentally upon the forces of molecular attraction between two sets of molecules. The forces of molecular attraction are commonly divided into two main groups.

The first broad class involves chemical bonds (primary bonds), which are usually classified as three types to include:

- Ionic-common bond, due to Coulomb electrostatic forces between oppositely charged ions derived from elements of widely different electronegativity.
- Covalent-electron pair bond, due to exchange forces between elements of similar electronegativities. This type of bonding is similar to the coordinate type bonds where the electrons in the bonding pair of both originate from one of the atoms.
- Metallic-bonding through the sharing of common electrons in an 'electron gas'. This occurs only for the least electronegative elements.

The second broad class to non-covalent type of bonding involves physical bonds (secondary bonds or van der Waals' forces), which are considered less important than chemical bonds. They are:

- Keesom dipole-dipole forces (orientation effects)-molecules which have permanent dipoles will have a mutual attraction and will cause a mutual alignment.
- Debye dipole-molecular forces (induction effect)-Here, a molecule with a permanent dipole moment will induce a dipole in a neighboring molecule by polarization.
- London molecule-molecule forces (dispersion effect)-this is a completely general interaction occurring between any two molecules (or atoms) which are in close proximity, irrespective of their permanent dipoles. Although a molecule may have a zero dipole, because over a period of time the electron arrangement is symmetrical, there will be instantaneous dipoles arising from the motion of the electrons due to the zero-point energy. This will cause induced dipole in phase. (Alner, 1963)

5.2. Adhesive Sorption.

Adhesives also have the ability to sorb gases and vapors. This sorption phenomenon can be divided into two types, namely physical and chemical. Physical sorption is caused by dispersion and coulombic forces, which are termed van der Waals'forces. Dispersion forces act between all atoms or molecules of matter, so that sorption of any gas on any solid can be brought about by dispersion forces.

Chemisorption is more specific in nature than physical sorption. It is due to the sharing of elecrons between the solid and the molecule or atom of the vapor. Chemisorbed gases are much more tightly bound than physically sorbed ones, and can usually be driven off only by exposing them to vacuum at high temperature. (Alner, 1963)

5.3. Polyurethane

Polyurethanes are a family of thermoset polymers containing urethane groups formed by the reaction of isocyanates and the hydroxyl groups of a prepolymer. There are a large number of combinations involving different isocyanates and a variety of polyols, such as polyesters and polyethers. In packaging, the most important use of polyurethanes is the lamination of flexible films. The most important cross-linked mechanisms are:

a. Two part adhesive systems where an isocynanate component forms one part and a polyol the other. Such systems give high resistances but have the disadvantage of limited pot life when mixed. They can be solvent-based or carrier-free liquids.

b. Blocked isocyanate. The isocyanate group can be blocked with another chemical group so that it can be combined with the polyol and remain stable. When heated the isocyanate unblocks and reacts. These types can be 100% solids, solvent-based or aqueous.

c. Moisture cure. Isocyanates react with any chemical which contains OH groups, including water. This provides a neat mechanism of cross-linking if the adhesive can be made entirely from dry ingredients and applied without contacting moisture. After application, moisture from the air or from the substrate causes cross-linking. Clearly these types cannot be water-based but can be either a solvent-based liquid or hot melt. In theory the latter is the ideal hot melt because the cross-link corrects the major disadvantage of hot melt : poor heat resistant of their bonds. In particular it is difficult to avoid premature cross-linking.

At present, solvent-based products dominate because of their superior wetting of difficult surfaces, better adhesion and higher chemical and heat resistance, but great advances are being made in water-based products. (Booth, 1990)

6. Permeation Studies

Food packages may gain or loss moisture, volatile food components, atmospheric gases, or contaminants by permeation through the package. Permeation through a polymeric packaging material occurs by a complex process including the following three steps:

- the permeating substance must dissolve in the material
- the permeating substance must diffuse through the material

- the permeating substance must leave the material by a reversal of the process that caused it to dissolve in the first step.

These three steps are described clearly by Figure 2:

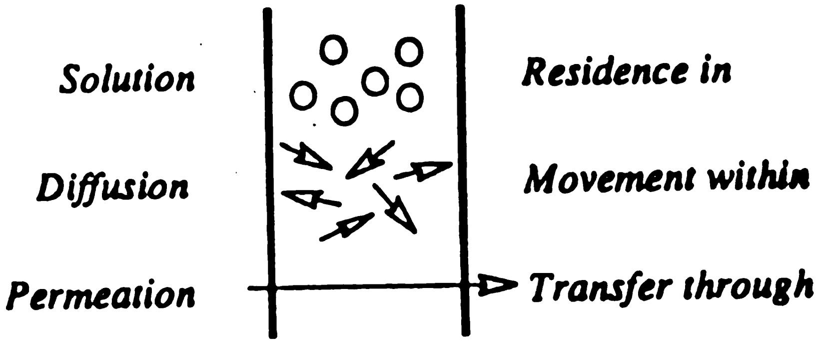


Figure 2. Concept of Solution, Diffusion, and Permeation

Permeation is the transport of a substance through a substrate, involving absorption and condensation on one surface (i.e. solution), diffusion to the other surface, and dissolution from the other side. The rate of permeation is usually described by the permeability coefficient ($\overline{P}$), expressed as the quantity of permeant that passes through a material of a unit thickness, unit time, unit surface area for a given concentration of the permeant. The permeability coefficient ($\overline{P}$) can be determined from the relationship: (Crank, 1968).

$$\bar{P} = D \bullet S \qquad (1)$$

where, D is diffusion coefficient

S is solubility coefficient

D is the diffusion coefficient which describes the process of movement of a substance within itself or another substance, usually expressed as length²/unit time. Diffusion creates a concentration gradient in the substrate, with the highest concentration at the surface of entry. The dimensions of diffusion can be deduced from the expression of Fick's Law:

$$J = -D(\partial c / \partial x) \qquad (2)$$

where, J = flux

c = concentration

x = distance of the front from the origin

By definition, the amount of permeant retained per unit volume of the polymer ($\partial J / \partial x$) is equal to the rate of change of concentration with time:

$$\frac{\partial J}{\partial x} = \frac{-\partial c}{\partial t} \qquad (3)$$

If Eq. (2) is substituted into Eq. (3), then:

$$\frac{\partial J}{\partial x} = \frac{\partial}{\partial x}\left[-D\frac{\partial c}{\partial x}\right] = \frac{\partial c}{\partial t} \qquad (4)$$

And with rearrangement of the terms:

$$\frac{\partial c}{\partial t} = -D\frac{\partial^2 c}{\partial^2 x} \tag{5}$$

Eq.(5) is Fick's second law of diffusion and is applicable under conditions where diffusion is limited to the cross-direction and D is independent of concentration (Robertson, 1992).

Gas concentrations are usually expressed in terms of the pressure of the gas above each surface. These quantities may be related to Henry's law which describes a linear relationship between the concentration of the penetrate in the polymer and the penetrant concentration in the gas or vapor phase in contact with the polymer(Liu, 1986).

$$C = \Delta P \bullet S \tag{6}$$

where, C = concentration of the penetrant in the polymer
ΔP = concentration of the permeant in the gas phase
S = solubility coefficient

S is the solubility coefficient of the permeant in the polymer, expressed as the amount of permeant sorbed in the polymer matrix per gram or volume of polymer per unit pressure gradient.

The major contributing factors to the mechanism of diffusion include polymer morphology and the ability of polymer chain segments to experience random movement. With respect to polymer morphology, permeant molecules can only penetrate through the amorphous region of the polymer bulk phase, with the crystalline domains considered unaccessible. Above the glass transition temperature (Tg), polymer chain segments experience vibrational, rotational and translational motions that continually create temporary void volume domains within the polymer matrix and penetrant molecules move through the polymer matrix by formation of those voids.

Factors influencing the transmission rate of a permeant gas or vapor through a polymer membrane include: (Huang *et al.* 1968).

- molecular size, shape and physico-chemical nature of the permeant
- the nature of the polymer including morphology and molecular motion of the polymer
- temperature
- permeant composition / concentration

The glass transition temperature (Tg), which is an important factor with respect to the mass transfer process marks the transition from a "glassy" polymer state to a "leathery" polymer physical state. The increase in polymer chain segmental mobility above the glass transition temperature, significantly corresponds with an increase in permeability and diffusion rates.

Small diffusant molecules, such as oxygen, nitrogen and carbon dioxide, have almost no effect on the polymer molecules, while sorbed into the polymer matrix. Their agitations are relatively rapid compared to the agitations of the polymer chains (Meares, 1965). On the other hand, organic vapor molecules are much larger than oxygen, nitrogen, and carbon dioxide molecules and can be even larger than polymer chain segments. Therefore, the diffusion of organic compounds is a more complicated process, which depends on the molecular motion of both the polymer and diffusant molecules. Organic molecules may also have greater solubility in the polymer. These effects (i.e. molecular motion and solubility) result in swelling of the polymer by sorbed organic molecules in the polymer matrix. Once the organic molecules are sorbed by the polymer, they may act as a plasticizer which decreases the glass transition temperature and increases the polymer's segmental motion at all temperatures. This can result in further plasticization and higher permeability rate, or a poor barrier (Meares, 1965).

In order to meet many of the barrier requirements of food products, multilayer laminations are currently used to provide the required gas and vapor transmission rates. For example, Saran® and ethylene vinyl alcohol copolymers are typically incorporated into laminate structures to provide good oxygen barrier properties, while LDPE provides a good barrier to water vapor. Polyethylene terephthalate (PET) is commonly used in multilayer structures to provide physical strength.

The contribution of the individual layers of a multilayer laminate to the permeability of the resultant structure can be combined to give the following expression and the derivations were shown in Appendix III.

$$\frac{L_T}{P_T} = \frac{L_1}{P_1} + \frac{L_2}{P_2} + \frac{L_3}{P_3} \tag{7}$$

$$P_T = \frac{L_T}{\sum_{i=0}^{i=n} \frac{L_i}{P_i}} \tag{8}$$

MATERIALS AND METHODS

MATERIALS

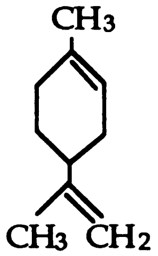
1. Adhesive

The urethane based adhesive system, Adcote 548/coreactant F, which was used in this study, is a commercially available adhesive system supplied by Morton International Co. (Chicago, IL 60606)(The technical bulletin for Adcote 548 Adhesive is presented in Appendix V). Methyl ethyl ketone (MEK)($CH_3COCH_2CH_3$, b.p.=79-80 °C) was used as the solvent for mixing Adcote 548 and coreactant F, and for diluting the adhesive.

2. Sorbates and Solvent

Table 1. Description of Sorbates and Solvent Used for This Study

Organics	Molecular Weight	Boiling Point (°C)	Density (g/ml)	Structure
Acetonitrile (Solvent)	41	82	0.775-0.780	CH_3CN
Hexanal	100	131	0.834	$CH_3(CH_2)_4CHO$

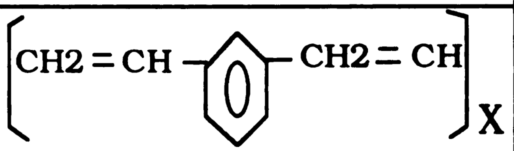
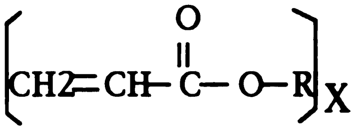
Ethyl Acetate	88	76.7-77.7	0.893-0.895	$CH_3COOC_2H_5$
Limonene	136	175.5-176	0.840	

3. Sorbents

The 6 types of sorbents were mixed with the adhesive in the ratio of 95:5 weight percent (adhesive : sorbent).

Table 2. Sorbents Tested

Sorbents	**Formula**	**Supply Company**
Aluminum Oxide	Al_2O_3 (79-96%) Na_2O (0.01-0.2%) Amorphous SiO_2 (0.01-0.2%) Fe_2O_3 (0.01-0.03%) Loss on Ignition(water) (3-20%)	Scientific Absorbents Inc.
Synthetic Amorphous Silica Gel	$SiO_2 \bullet xH_2O + CoCl_2$	Alltech Associates, Inc.

Florisil, Magnesium silicate	$MgO \bullet 3.75\ SiO_2(X)\ H_2O$	U. S. Silica Co.
Amberlite XAD-4 Divinyl benzene		Rohm and Haas Co.
Amberlite XAD-7 Acrylic ester	 $[CH2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}R]_X$	Rohm and Haas Co.
Tenax-TA (porous polymer) Poly(2,6-Diphenyl-p-phenylene oxide	$[C_6H_4O]x$	Alltech Associates, Inc.

4. Aluminum Foil

Heavy Duty Kaiser Aluminum Foil (Aluminum and Chemical Corporation, Packaging Division, 300 Lakeside drive., Oakland, CA 94643). The thickness of the aluminum foil is 1.1 mil.

5. Saran-F Resin

Saran* F-310 barrier polymer is a copolymer of vinylidene chloride, acrylonitrile, and methyl methacrylate.

Table 3. The Properties of Saran® F-310 Resin

Properties	Values	
Physical Properties		
Specific Gravity	1.6	
Performance Properties[f]	Coating Weights	
	2.2 g/m²	4 g/m²
Oxygen Permeance[b]	1.5	0.35
Water Vapor Transmission Rate[c]	43	20
Water Vapor Transmission Rate[d]	2.8	1.3
Minimum Heat Seat Temperature[e]	--	130

[a] Complies with requirements of FDA for use as a component of articles in contact with food.

[b] cc/100 in²•24hrs•atm @ 73°F (23°C), 75% RH (ASTM D-1434)

[c] g/meter²•24 hrs @ 100°F (38°C), 90% RH

[d] g/100 in²•24 hrs @ 100°F (38°C), 90% RH

[e] °C, 1 second dwell, 5 psi

[f] Tested on P.E.T. substrate

- Recommended Dissolving Conditions

The Saran® F-resin was dissolved in 65% methyl ethyl ketone and 35% toluene to give a clear solution of 20% F-resin on a dry weight basis at 23 °C for one hour.

6. Oriented Polypropylene (OPP)

A 2mil biaxially oriented polypropylene film, provided by the Mobil Chemical Company (Macedon, New York 14502), was used in these studies. The level of elongation was 420% (

machine direction) and 800% (cross direction), based on the initial film dimensions. The percent crystallinity, calculated from heat of fusion, was 45.7%.

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Experimental Methods

1. Gas Chromatographic Analyses

The absorption studies were performed by gas chromatography (GC) analysis (Hewlett Packard, Model 5890A, Avondale, PA). The gas chromatographic conditions were as follows:

A Hewlett-Packard Model 5890A gas chromatograph, equipped with dual flame ionization detectors and interfaced to a Hewlett-Packard Model 3395 integrator was used. A setting of 1 minute purge on was utilized for all analyses.

<u>GC Model 5890A</u>

Column : Supelcowax™ (Supleco Co., Bellefone, PA)
fused silica capillary
polar bonded stationary phase
60 meter in length
0.25 mm inner diameter

Carrier gas : Helium at 2.21 ml/min. flow rate

Temperature : Injection port temperature - 220 °C
Detector temperature - 250 °C
Temperature program :
Initial temperature - 40 °C
Initial time - 1 minute
Rate - 5 °C/min.

Final temperature - 150 °C

Final time - 10 minute

Integrator Model 3395

Zero : 0, -0.5

Attenuation : 6

Chart speed : 0.5 cm/min.

Peak width : 0.04

Threshold : 0

Area response reject : 0

The approximate retention times for each probe compound were determined to be the following:

Hexanal - 12.3 ± 0.3 minutes

Ethyl Acetate - 6.1 ± 0.3 minutes

Limonene - 25.7 ± 0.2 minutes

The standard calibration curves for hexanal, ethyl acetate, and limonene are presented in Appendix I.

2. Sorption Study

2.1. Preparation of Saturated Sorbate Vapors

To provide a known concentration of sorbate for the sorption studies, the following procedure was followed. 20 ml of the respective liquid sorbate were added to 150 ml septa seal vials equipped with a Teflon faced silicone septum and aluminum crimp cap. The vial was sealed and allowed to equilibrate at 23±2 °C. The saturation vapor concentrations for hexanal, ethyl acetate, and limonene were 3.21, 114.25, and 0.73 ppm(wt/v),respectively. In performing sorption studies, a 500µl sample was withdrawn from the headspace of the equilibrated sorbate standards with a 500 µl Hamilton 1725 Economical Gastight Syringe (Hamilton Co., Reno, NV) and injected directly into the sorption cells.

2.2. Procedure Used to Evaluate the Seal Integrity of the Sorption Cell Systems:

Three types of sorption cells were evaluated, and are described below:

a. 450 ml Pint Jar with Screw Cap. The cell design is presented in Figure 3. As shown, sampling was achieved through a sampling septum affixed to the jar lid.
b. 250 ml Serum Type Vial with Mininert Valve (Pierce, Rockford, IL.) and the cell design is shown in Figure 4.
c. 150 ml Sure/Seal Oxford Bottle with Crown Cap and Teflon Septa (Aldrich Chemical Co.). The cell design is presented in Figure 5. The Aldrich Sure/Seal system consists of a Teflon faced rubber liner and crown cap, while is hermetically sealed by a hand capper designed for this system (See Figure 6.).

To evaluate the seal integrity of the respective sorption cell systems, a known amount (500 µl) of saturated sorbate vapor was added to the sorption cell through the sampling port. Headspace samples (200 µl) were withdrawn from the sorption cells at intervals of 0, 24, and 48 hours

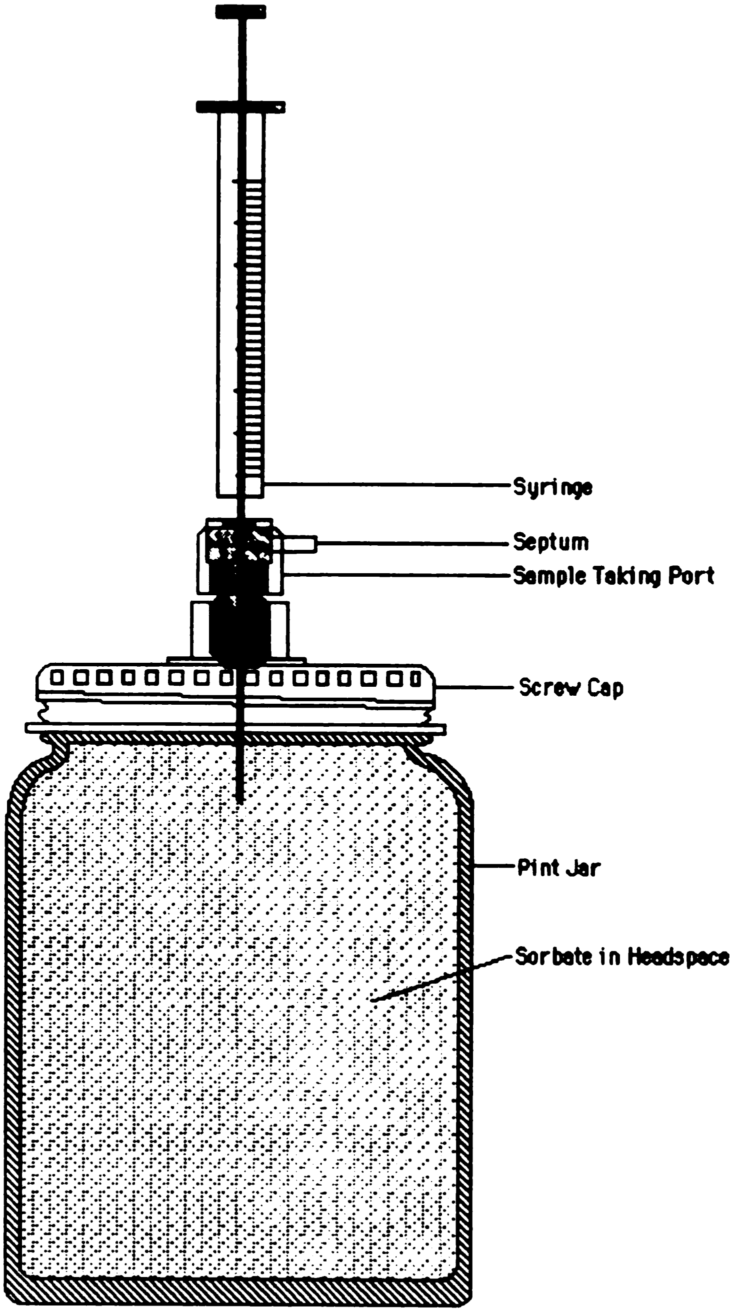

Figure 3. 450ml Pint Jar with Screw Cap

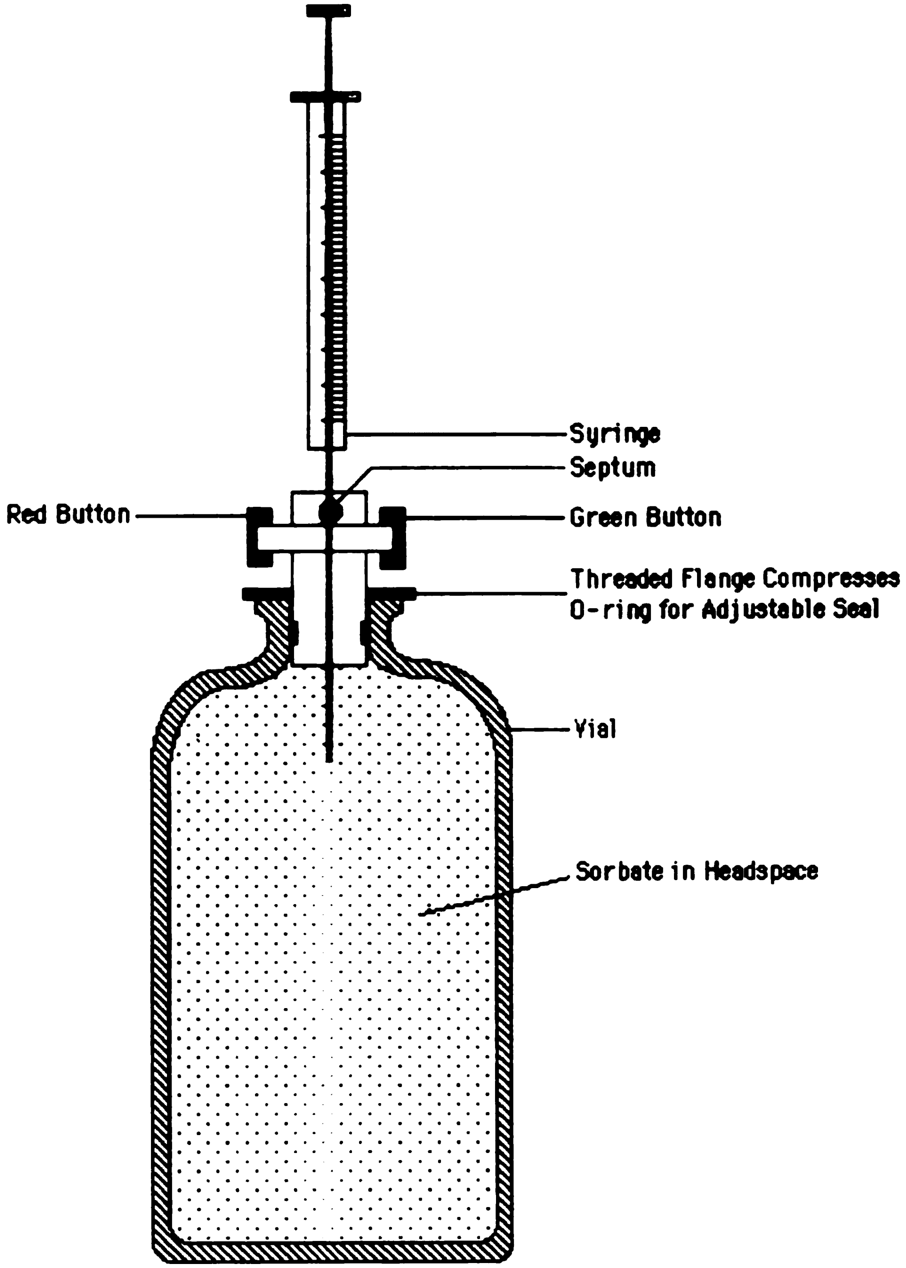

Figure 4. 250ml Serum Vial with Mininert Valve

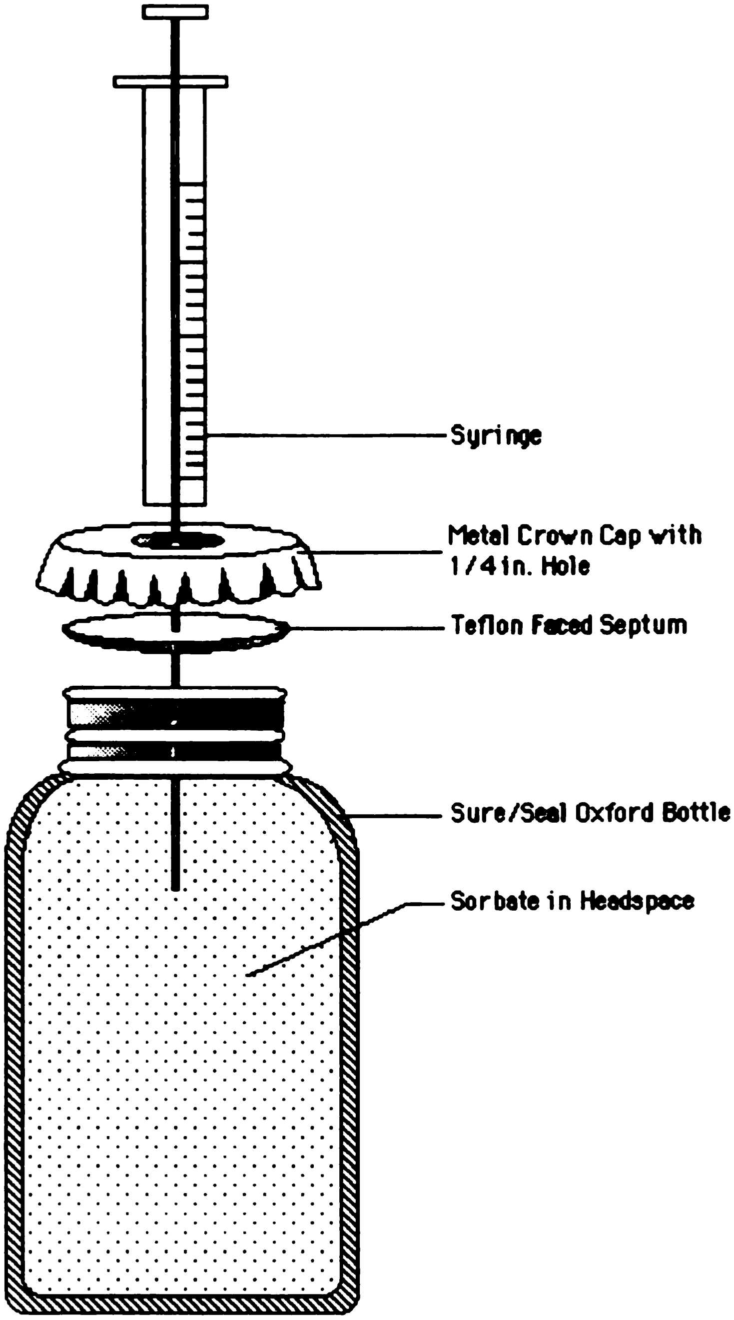

Figure 5. Sorption Cell System : Sure/Seal Oxford with Crown Cap and Teflon Faced Septum

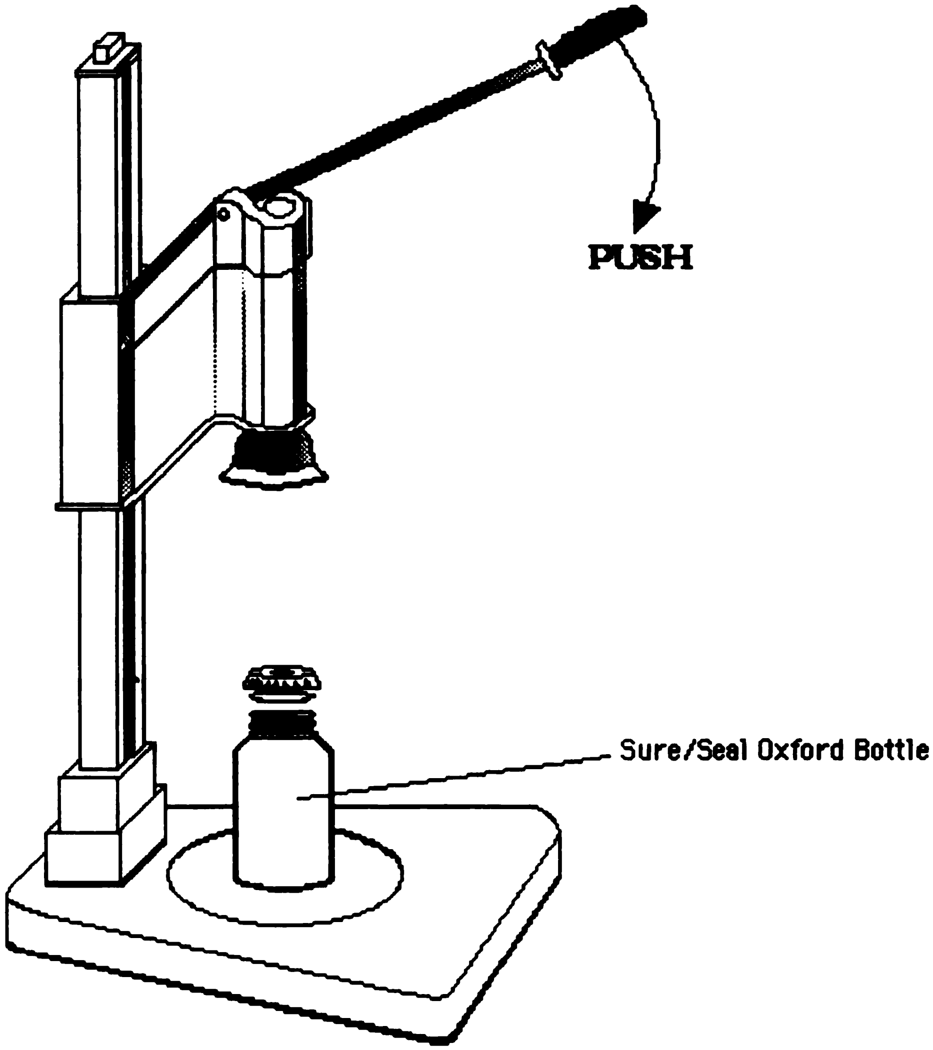

Figure 6. Capper for Sure/Seal Oxford Bottle

and injected directly into the gas chromatograph for quantification.

For all sorption studies, the sorption cells were stored at 23 ± 2 °C. The concentration of sorbate was determined as a function of time and reported as relative percent remaining. All sorption studies were carried out with the sure/seal system because of its lower level of leakage in 48 hours seal integrity test.

2.3. Test Procedure Developed to Evaluate the Sorption Capacity of the Sorbent

The sorbents (0.2 g) was added directly to the sorption cell and the system sealed. A known amount (500 μl) of saturated sorbate vapor was added to the sorption cell through the sampling port. Headspace samples (200 μl) were withdrawn from the sorption cells at intervals of 0, 24, and 48 hours and injected directly into the gas chromatograph for quantification.

500 μl saturated hexanal vapor is 1.3 mg.

500 μl saturated ethyl acetate vapor is 58.8 mg.

500 μl saturated limonene vapor is 0.3 mg.

2.4. Procedure to Evaluate the Adhesive Sorption Capacity

The Adcote 548 adhesive was formulated by mixing the Adcote 548 and coreactant-F in a 10 to 1, weight/weight basis. The adhesive system was diluted with methyl ethyl ketone to give a solution of 43% solids on a dry weight basis. A metering Rod (No.34) was used to prepare adhesive drawdowns on aluminum foil. After coating the adhesive layer onto an aluminum foil sheet, the coated aluminum foil was placed under the hood for 1 hour to evaporate the bulk of the solvent. The adhesive coating was further dried by placing the coated sample in a 60 °C oven for 24 hours.

To evaluate the sorption capacity of the cured Adcote 548 adhesive, a 2 cm x 5 cm film sample were added into the sorption cell system. A known amount (500 μl) of saturated sorbate vapor was added to the sorption cell through the sampling port. Headspace samples (200 μl) were withdrawn from the sorption cells at intervals of 0, 24, and 48 hours and injected directly into the gas chromatograph for quantification.

2.5. Procedure Developed to Evaluate the Sorptive Capacity of the Adhesive Matrix Dispersed Sorbent

The Adcote 548 adhesive was formulated by mixing the Adcote 548 and coreactant-F in a 10 to 1, weight/weight basis. The adhesive system was diluted with methyl ethyl ketone to give a solution of 43% solids on a dry weight basis. The adhesive solution was formulated with 10% absorbent added on a weight/weight basis to provide the absorbent impregnated adhesive layer. The loading level of the absorbent was estimated to be 1.3 mg sorbent/10 cm^2 surface area adhesive or 0.04 g sorbent/g adhesive. A No.34 Metering Rod was used to prepare adhesive drawdowns on aluminum foil. After coating the absorbent impregnated adhesive layer onto an aluminum foil sheet, the coated aluminum foil was placed under the hood for 1 hour to evaporate the bulk of the solvent. The adhesive coating was further dried by placing the coated sample in a 60 °C oven for 24 hours.

To evaluate the sorption capacity of the adhesive matrix dispersed sorbents, a 2 cm x 5 cm coated aluminum foil sample was added into the sorption cell system. A known amount (500 μl) of saturated sorbate vapor was added to the sorption cell through the sampling port. Headspace samples (200 μl) were withdrawn from the sorption cells at intervals of 0, 24, and 48 hours and injected directly into the gas chromatograph for quantification.

The average thickness of the adhesive coating was 8.2 ± 0.5 mil, which was determined by optical microscope analysis. The micrograph is illustrated in Appendix II.

2.6. Preparation of the OPP / Absorbent Impregnated Adhesive / Saran® Laminate Film

The adhesive system was diluted with MEK to give a solution of 30% solids on a dry weight basis. The adhesive solution was also formulated with 16% Florisil absorbent added on a dry weight basis, to provide the absorbent impregnated adhesive layer. The loading level of Florisil was estimated to be 0.12 mg sorbent/cm^2 surface area adhesive or 0.05 g sorbent/g adhesive. The adhesive formulation without absorbent served as the control. A Metering Rod (No.10) was used to prepare adhesive drawdowns for both the control film and the test film, which were fabricated with the absorbent impregnated adhesive. After coating the adhesive layer onto the oriented polypropylene film, the coated samples were placed under the hood for one hour to evaporate the bulk of the solvent. The adhesive coating was further dried by placing the coated samples in a 60 °C oven for 24 hours.

After the adhesive layer was cured, the Saran® F-resin was dissolved in 65% MEK/35% toluene to give a solution of 20% F-resin on a dry weight basis. A Metering Rod (No.6) was used to coat the Saran® onto the adhesive layer. The absorbent impregnated OPP/Saran® film was first placed under the hood for one hour to evaporate the bulk of the solvent and further dried by placing the film in a 60 °C oven for 36 hours.

The average thickness of the adhesive coating was 0.77 ± 0.03 mil and the Saran® layer was 0.36 ± 0.01 mil, which was determined by optical microscope analysis. A representative micrograph is presented in Appendix II.

3. Permeation of the Sorbent Impregnated Laminate Structure

3.1. Permeation Test Method:

The permeation test system, employed in this study, was based on the quasi-isostatic method. Figure 7 presents a

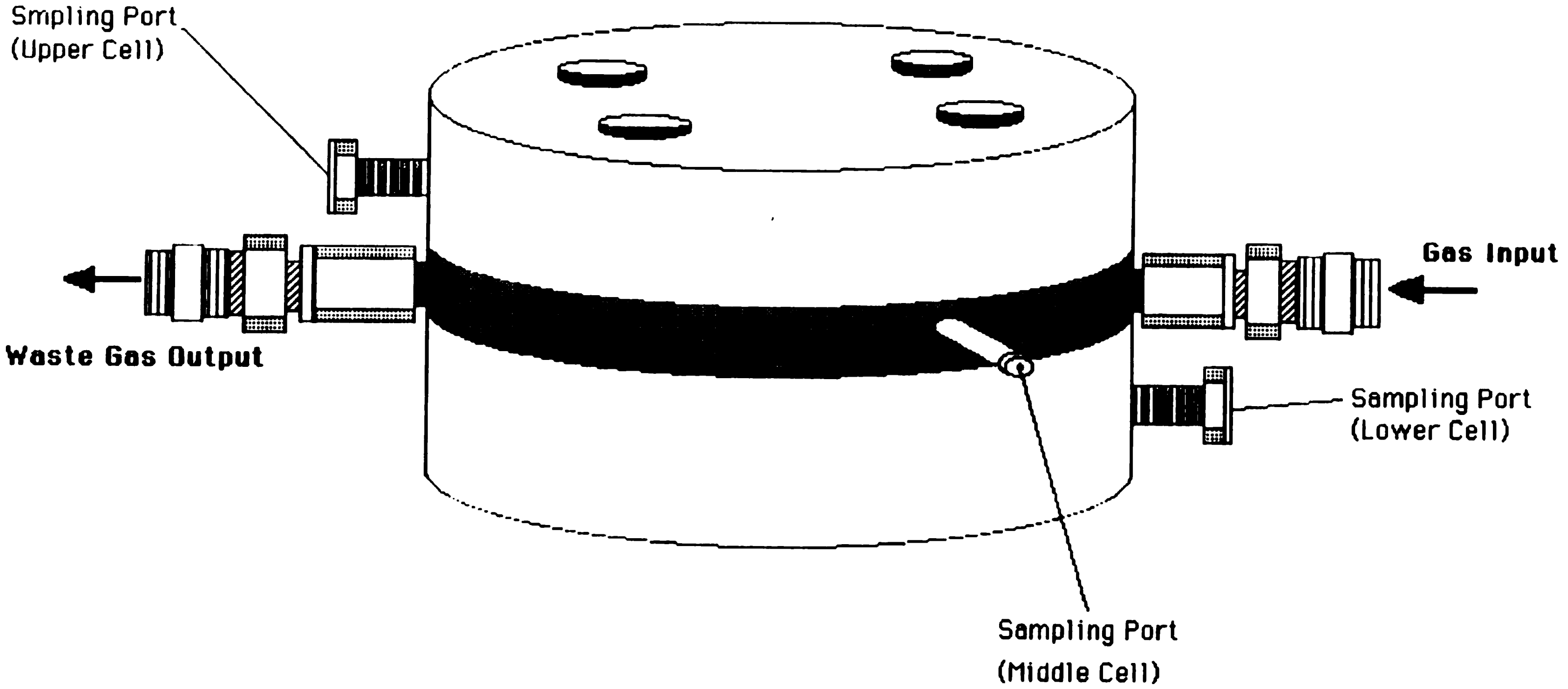

Figure 7. Permeation System

schematic diagram of the permeation test system. Permeability studies with limonene were carried out at 60 ± 2 °C with an average constant vapor concentration of 0.83 μg/ml, which was equivalent to 0.11 vapor activity.

The permeability cell, was comprised of two aluminum cell chambers and a hollow center ring. Each chamber was fitted with an inlet and outlet valve and a gas sampling port. The upper and lower cell chambers each had a volume of 50 ml. In operation, film samples were mounted in the cell such that the center ring effectively isolated the upper and lower cell chambers. A constant, low partial pressure of permeant vapor was then flowed continuously through the center cell chamber at a fixed constant flow rate (20 ml/min.). Based on this design, the permeability of two film specimens could be determined, concurrently. A constant concentration of permeant vapor was produced by bubbling nitrogen gas through the liquid permeant. This was carried out by assembling a vapor generator consisting of a gas washing bottle, with a fritted dispersion tube, containing the organic liquid.

3.2. Vapor Permeant Quantitation

The permeability rate through the film samples was determined by periodically removing samples (200 μl) from the cell's headspace with a gas tight syringe (500 μl Hamilton 1725 Economical Gastight Syringe, Hamilton Co., a

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Reno, NV) and immediately injecting the gas sample into a Hewlett Packard 5890A Gas Chromatograph (Baner, 1987).

3.3. Permeation Data Analysis

As the data are collected, they are plotted on a graph as total permeant accumulated in the headspace versus the elapsed time. The curve produced is the transmission profile curve. The steady state permeation region is the portion of the curve where there is a steady increase in permeant concentration with time, resulting in a straight line on the transmission profile curve. The slope of the linear portion is the organic vapor transmission rate or flux (Siegel *et al.*, 1970).

4. Analysis of Film Thickness by Optical Microscopy

Analysis of the film thickness of each layer on the absorbent impregnated OPP/Saran® film was carried out with an optical microscope Olympus BH-2. The photographs were taken with a Polaroid 545 Land Film Camera with Polaroid 57 PolaPan 4 x 5 instant sheet film. The sample preparation procedure was as followed:

(1). Cut out a 1 in x 1 in square film sample

(2). Cut the gel capsule in two sides and insert the film sample

(3). Fill gel capsule with polymethyl methacrylate (PMMA) gel and allow to cure

(4). After curing , place gel capsule and sample in a polishing block holder and fill entire holder with PMMA gel and allow this to cure

(5). Remove cured PMMA polishing block from holder and mount in the Streurs polishing vice

(6). Start with a 240 grit sand paper and polish for 1 min.

(7). Repeat step 6 with finer sand papers in the following order:

320
1000
2400
4000

(8). Mount the samples on a glass microscope slide under the microscope and photograph

(9). The samples were examined at 66 x magnification

5. Statistical Analysis

The integrity of the sorption cells and sorption of sorbents were analyzed using the analysis of variance (ANOVA) by Factorial program of the MSTAT microcomputer statistical program (Michigan State University, ver. 4.0, 1987)(Appendix III).

The differences between the absorbent and control group were determined and calculated by using the Dunnett's t-value. When a t (calculated) value is higher than the t_D

(tabulated) value, it indicates a statistically significant difference (*, $\alpha = 0.05$; **, $\alpha = 0.01$).

RESULTS AND DISCUSSION

1. Seal Integrity

Preliminary studies were carried out to evaluate the three sorption cell systems considered. The sorption cell systems were: (i)450 ml Pint Jar with closure; (ii) a serum vial with Mininert Valve, and (iii) sure/seal Oxford bottle with crown closure. The three sorption cell systems showed different degrees of seal integrity to hexanal as the sorbate.

The results showed minimum sorbate losses from the sure/seal Oxford bottle, while significant losses were found with the other two sorption cell systems considered. For example, with the sealed 450 ml Pint Jar, nearly 80% of the added hexanal was lost within 48 hours. For the Mininert valve/serum vial system, losses of hexanal ranged from 70-80%, after 48 hours storage at ambient temperature. The highest level of seal integrity was achieved with the sure/seal Oxford bottle, which maintained 93% to 99% of the added hexanal over the first 24 hours, and retained over 80% of the hexanal added after 48 hours. These findings are illustrated graphically in Figure 8, where the relative percent of hexanal remaining in the sorption cells is plotted as a function of storage time.

For ethyl acetate, the sure/seal system retained 75-83% of added sorbate after 48 hours (shown in Figure 9). For limonene, losses ranged from 5-10% after 48 hours storage at ambient temperature (shown in Figure 10). Based on these findings, all subsequent sorption studies were carried out with the sure/seal Oxford bottle system.

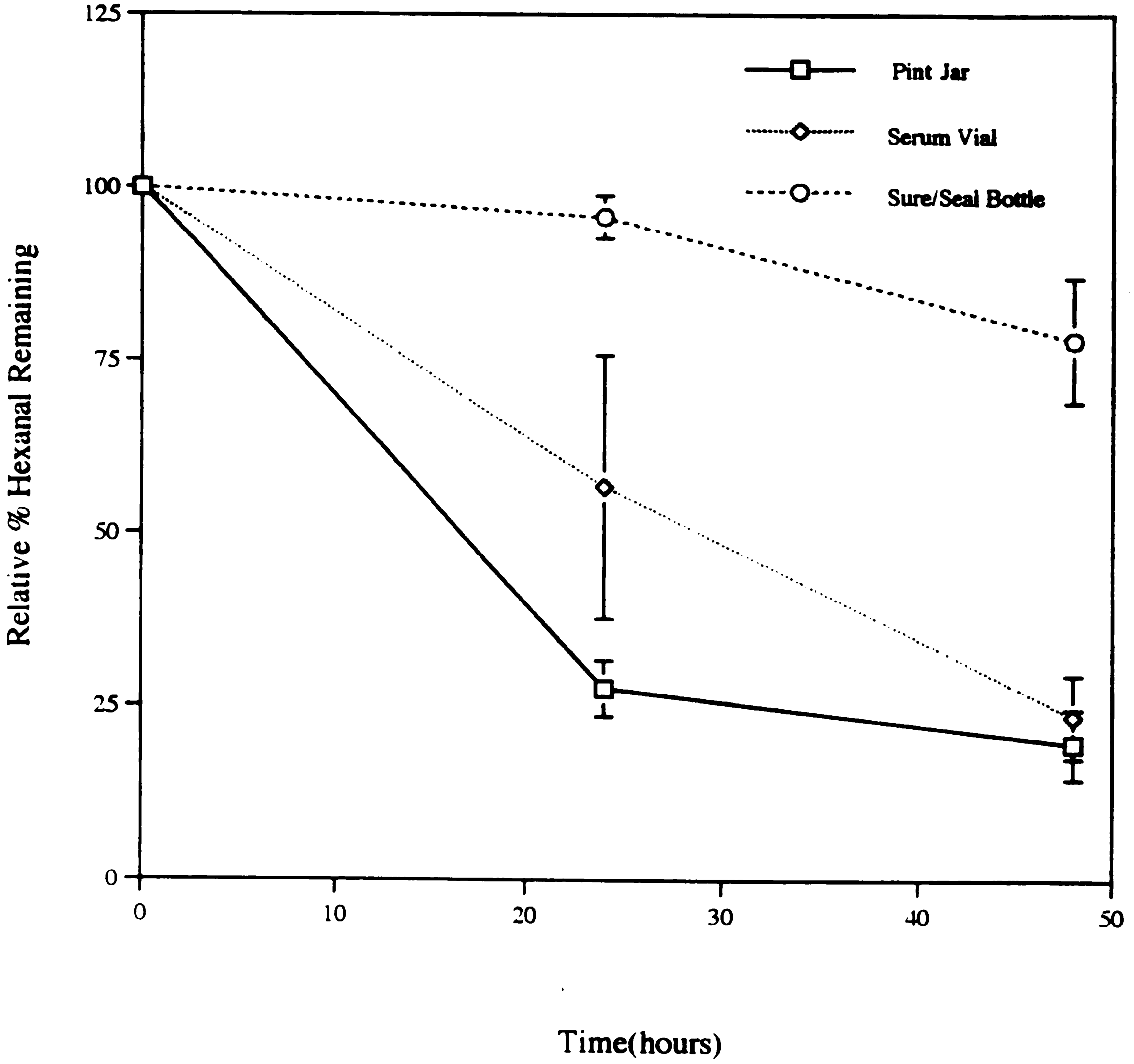


Figure 8. Seal Integrity - The Rate of Loss of Hexanal in
(a) 450ml Jar/Closure System
(b) Serum Vial with Mininert Valve System
(c) Sure/Seal Oxford Bottle System

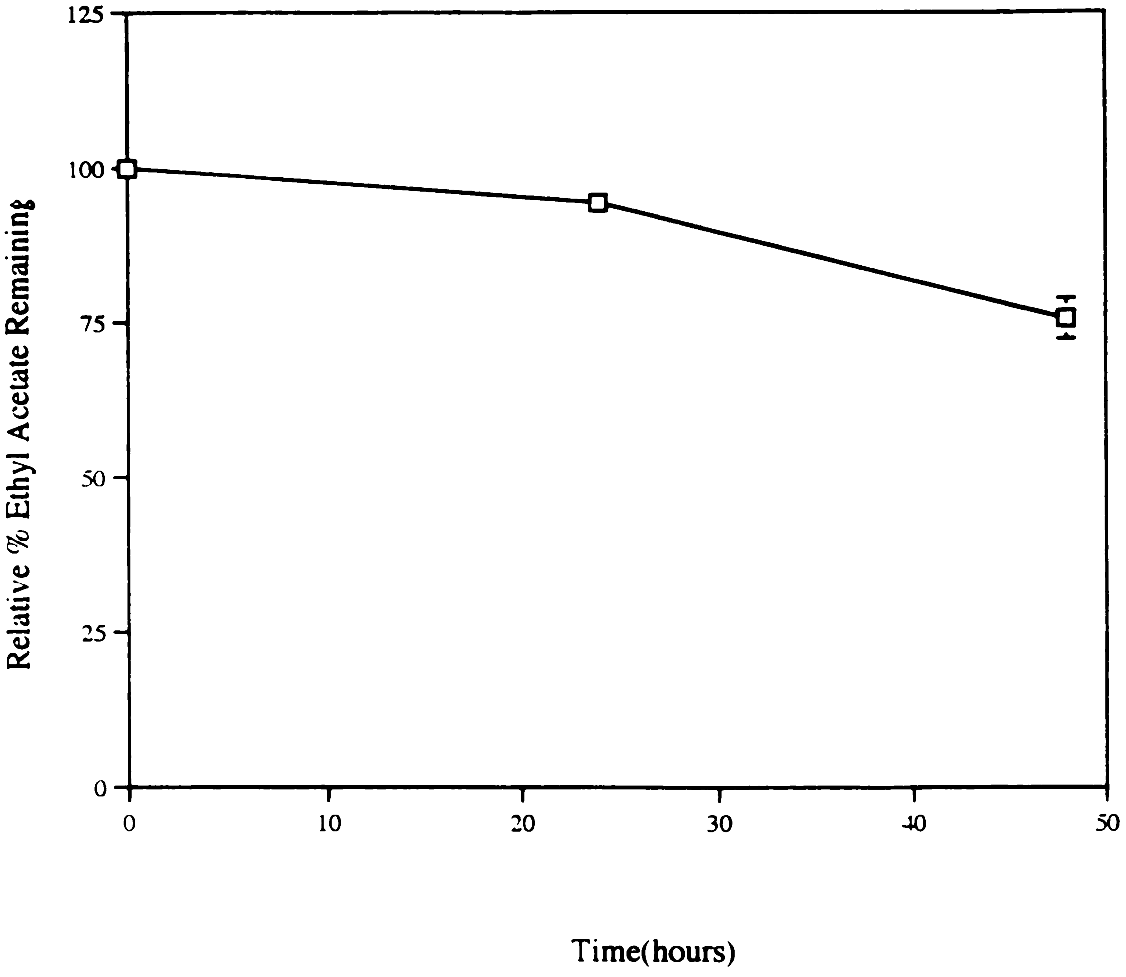


Figure 9. Seal Integrity of Ethyl Acetate for Sure/Seal Oxford Bottle System

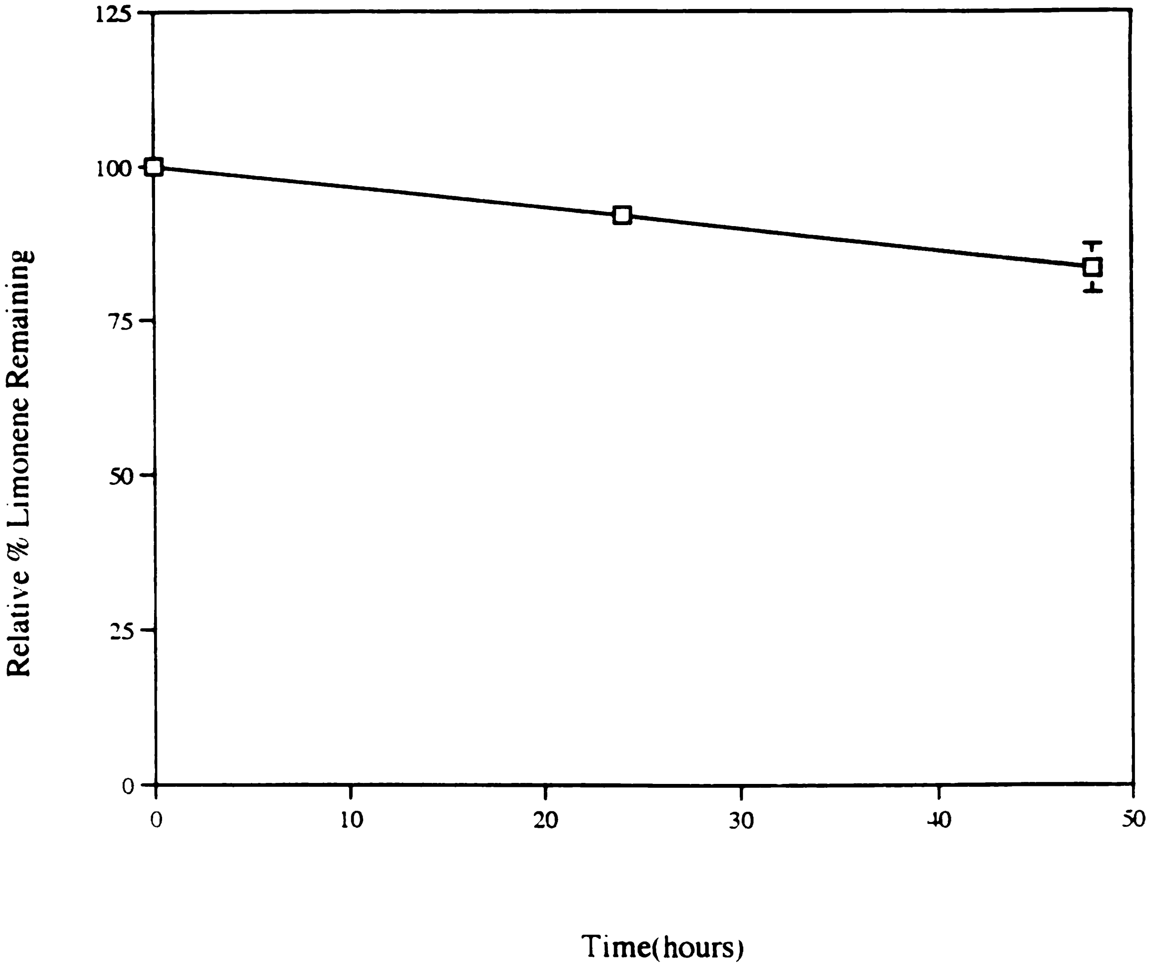


Figure 10. Seal Integrity of Limonene for Sure/Seal Oxford Bottle System

2. Sorbents Sorption Capacity

The results of the studies carried out to evaluate the sorptive capacity of a series of sorbents are summarized in Table 4, and presented graphically in the histograms shown in Figures 11-13 .

For hexanal, the results showed that the four sorbents, silica gel, Tenax-TA, Alumina super active I, and Florisil, all have high sorptive capacities for hexanal, with no detectable levels observed in the cell headspace following 24 hours storage at ambient temperature (shown in Figure 11). Amberlite XAD-4 also proved to be a highly efficient sorbent for hexanal, with near quantitative losses being observed after 48 hours storage at ambient temperature. Amberlite XAD-7 was found to be less effective as a sorbent for hexanal than the other sorbents evaluated.

For ethyl acetate, silica gel, Alumina super active I, and Florisil exhibited the highest sorption capacities. The sorption of ethyl acetate by Tenax-TA was also quite high. The sorption capacities of Amberlite XAD-4 and Amberlite XAD-7 were limited with the levels of ethyl acetate remaining after 48 hours at ambient temperature conditions, being 32 and 71%, respectively (shown in Figure 12).

For limonene as the sorbate, quantitative uptake was observed within 48 hours for the sorbents, silica gel, Florisil, Tenax-TA, and Amberlite XAD-7. Alumina super active I was also an effective sorbent, while Amberlite XAD-4 showed the lowest propensity to sorb limonene (shown in Figure 13).

The results of analysis of variance (ANOVA) for mean squares of sorbents is presented in Appendix IV. The results showed that the sorbents significantly sorb the sorbates, when compared to the sorption cell system without sorbent.

Table 4 . Sorption Capacity of Selected Sorbent System

Storage Time (hours)	Sorb- bents / Organics	Relative Percent Sorbate Remaining [(a)(b)]						
		Silica Gel	Alumina	Florisil	Tenax	XAD-4	XAD-7	Control
0	Hexanal	100%	100%	100%	100%	100%	100%	100%
24		0%	0%	0%	0%	2.1%	20.3%	95.6%
48		0%	0%	0%	0%	1.1%	20.3%	78.0%
0	Ethyl Acetate	100%	100%	100%	100%	100%	100%	100%
24		1.7%	2%	2.5%	4.4%	28.9%	81.6%	94.4%
48		0.1%	0%	0.5%	4.2%	32.3%	71.5%	75.6%
0	Limonene	100%	100%	100%	100%	100%	100%	100%
24		12.1%	5.5%	0%	0%	35.3%	0%	92.0%
48		0%	3.6%	0%	0%	26.6%	0%	83.3%

(a) Storage temperature = 21 ± 1°C

(b) Average of triplicate analysis

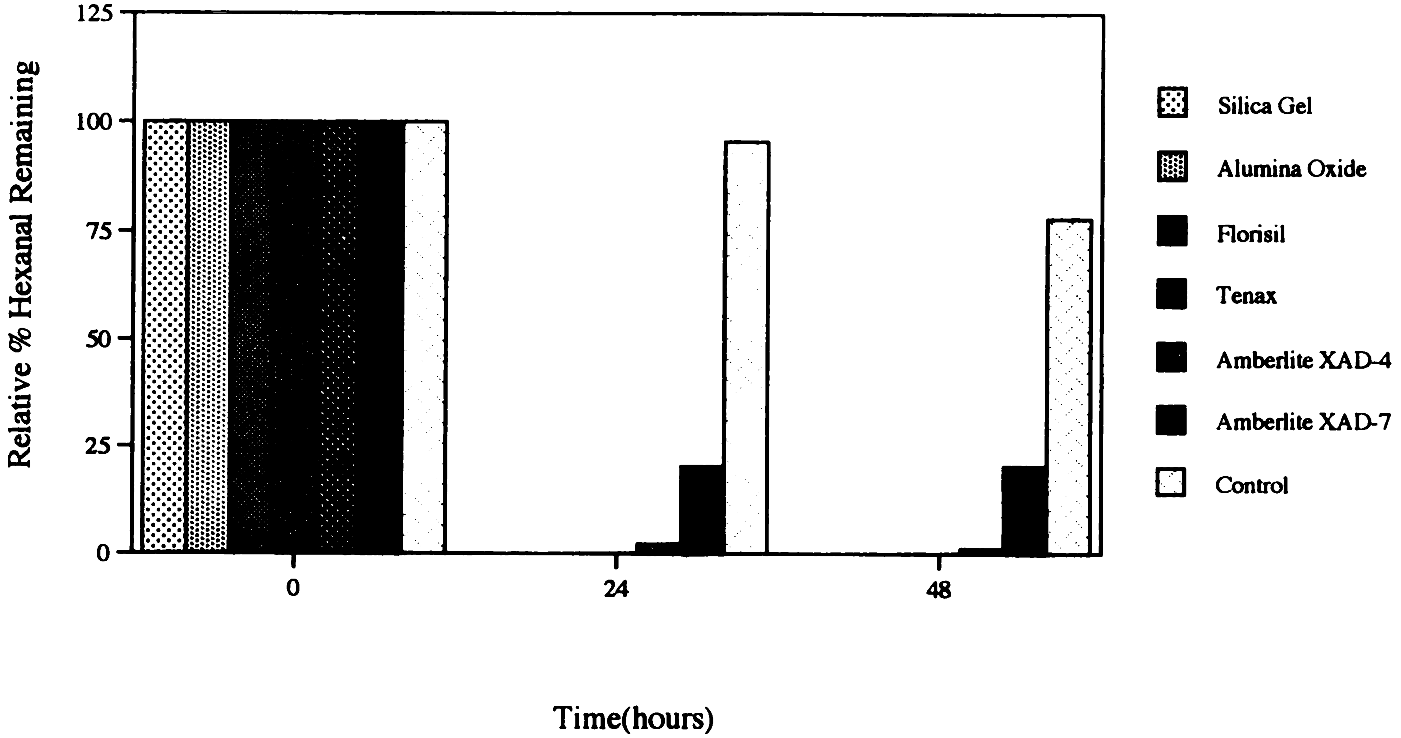


Figure 11. Sorption Capacity of Six Sorbents for Hexanal

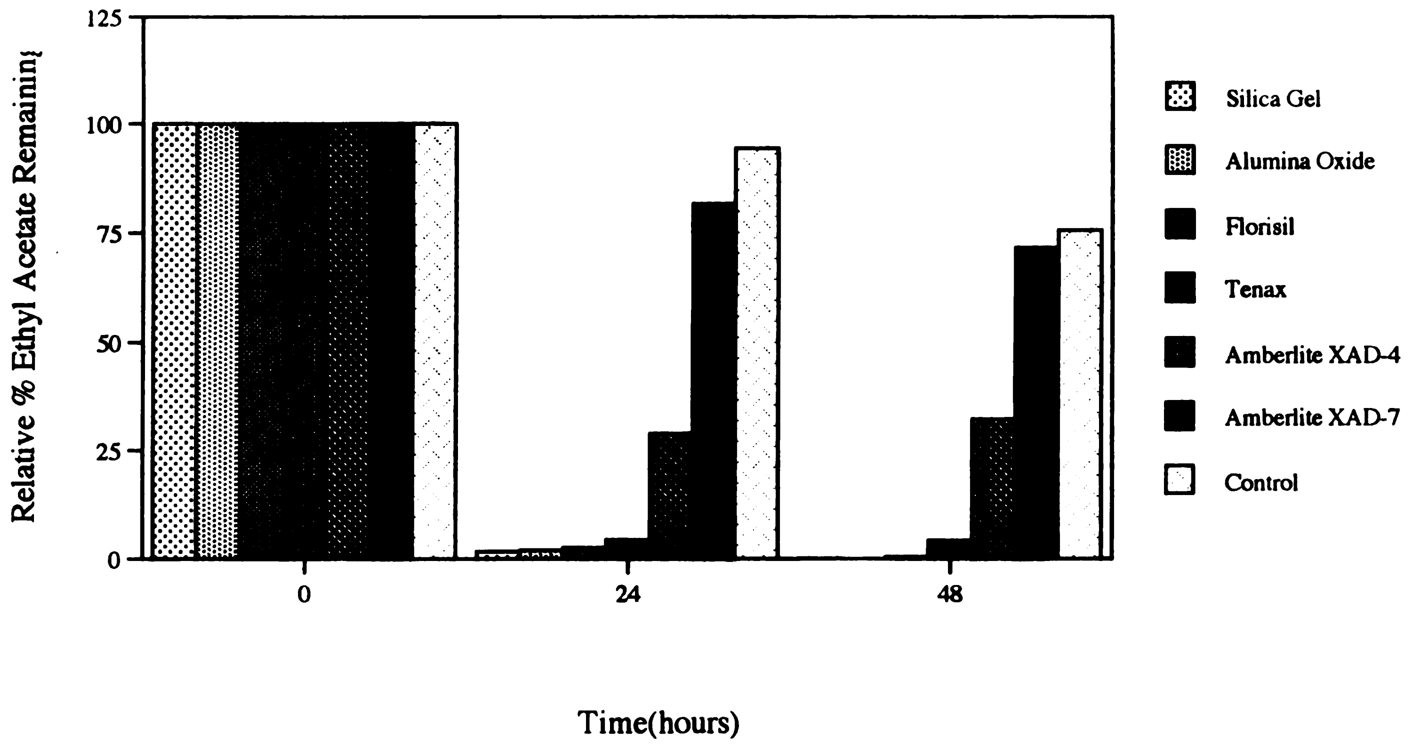


Figure 12. Sorption Capacity of Six Sorbents for Ethyl Acetate

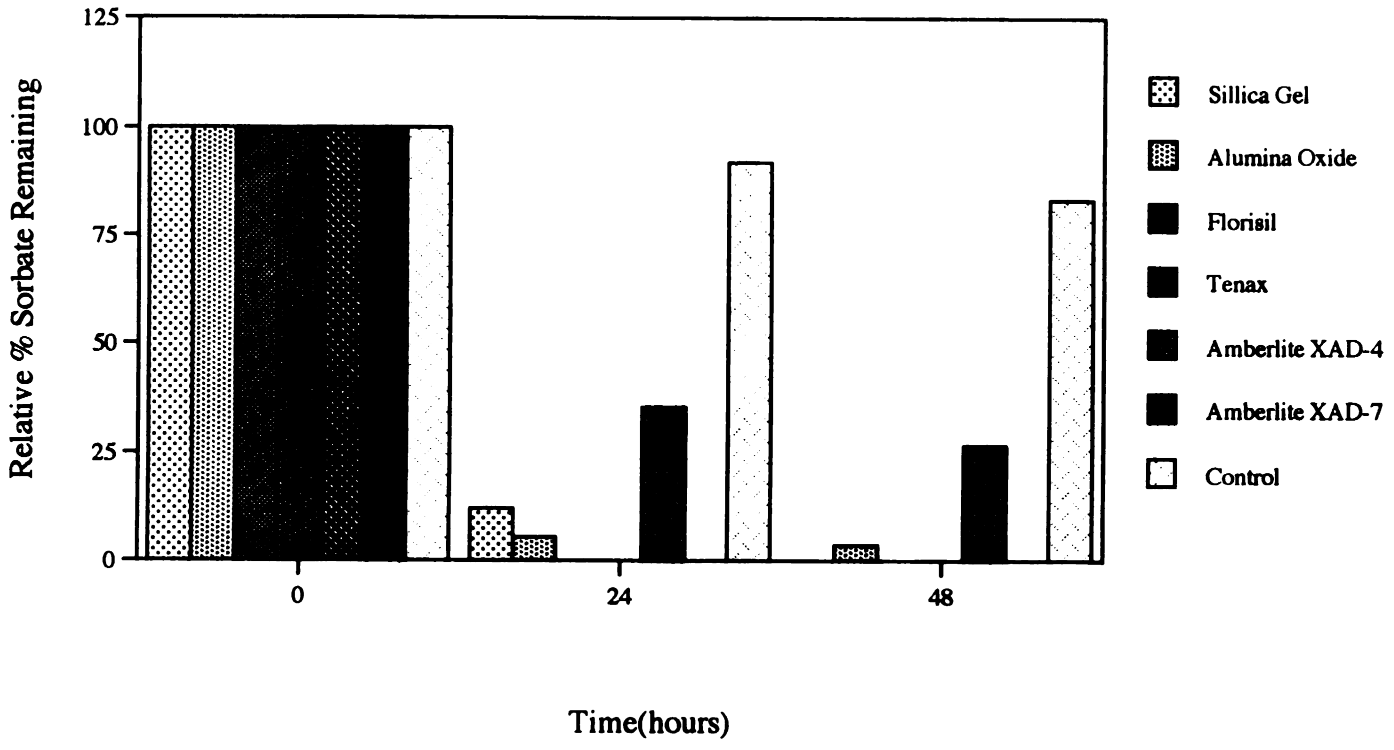


Figure 13. Sorption Capacity of Six Sorbents for Limonene

3. Adhesive Sorption Capacity

The sorption capacity of cured adhesive (Adcote 548), which had been coated onto aluminum foil, was evaluated for the three (3) test sorbate compounds. The results showed limited levels of sorption of the respective sorbates by the Adcote 548 adhesive system.

For hexanal approximately 68.9% of that initially added to the sorption cell remained after 24 hours and 59.2% after 48 hours (shown in Figure 14). For ethyl acetate, nearly 84.3% of the initially added sorbate remained after 24 hours and 73.7% after 48 hours.(shown in Figure 15). For limonene, 59.0% of that initially added to the sorption cell remained after 24 hours and 52.6% after 48 hours (shown in Figure 16).

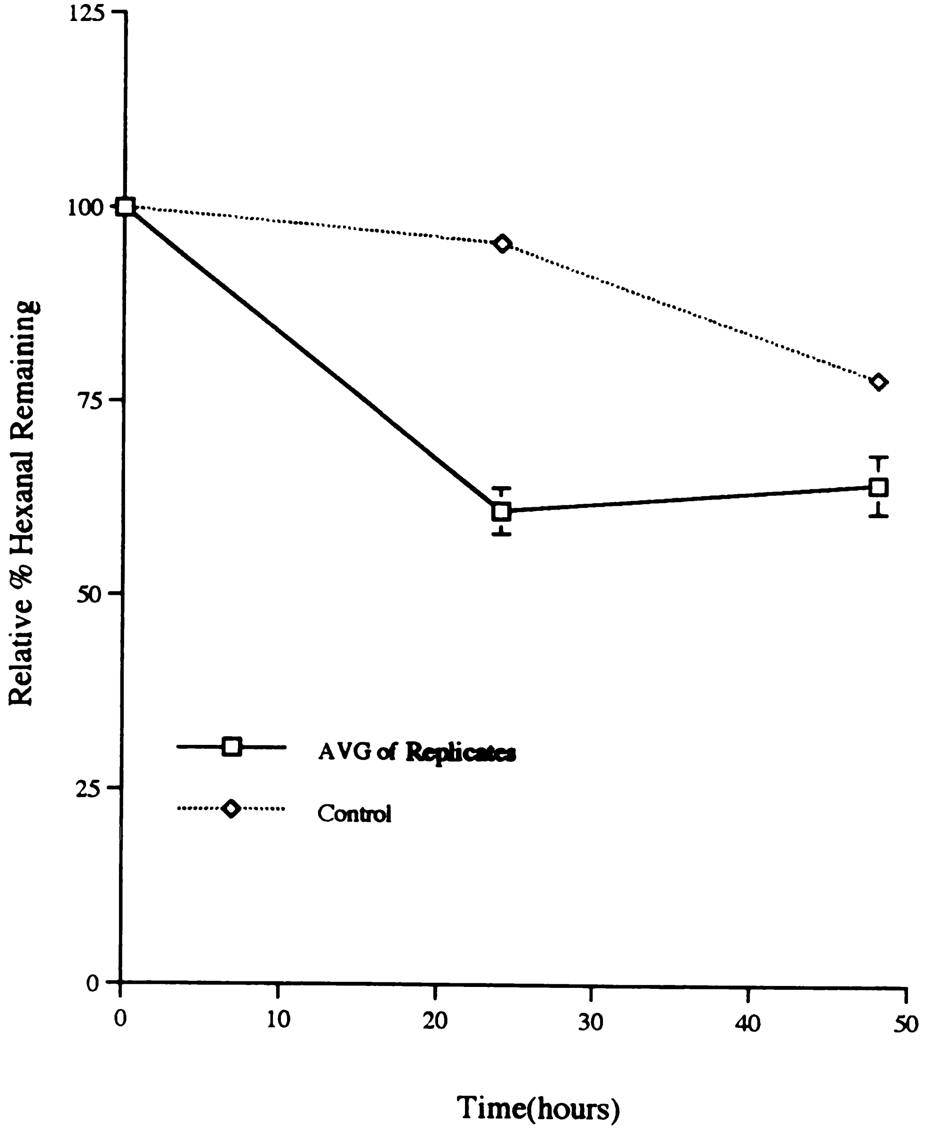


Figure 14. Sorption Capacity of Adcote 548 Adhesive for Hexanal

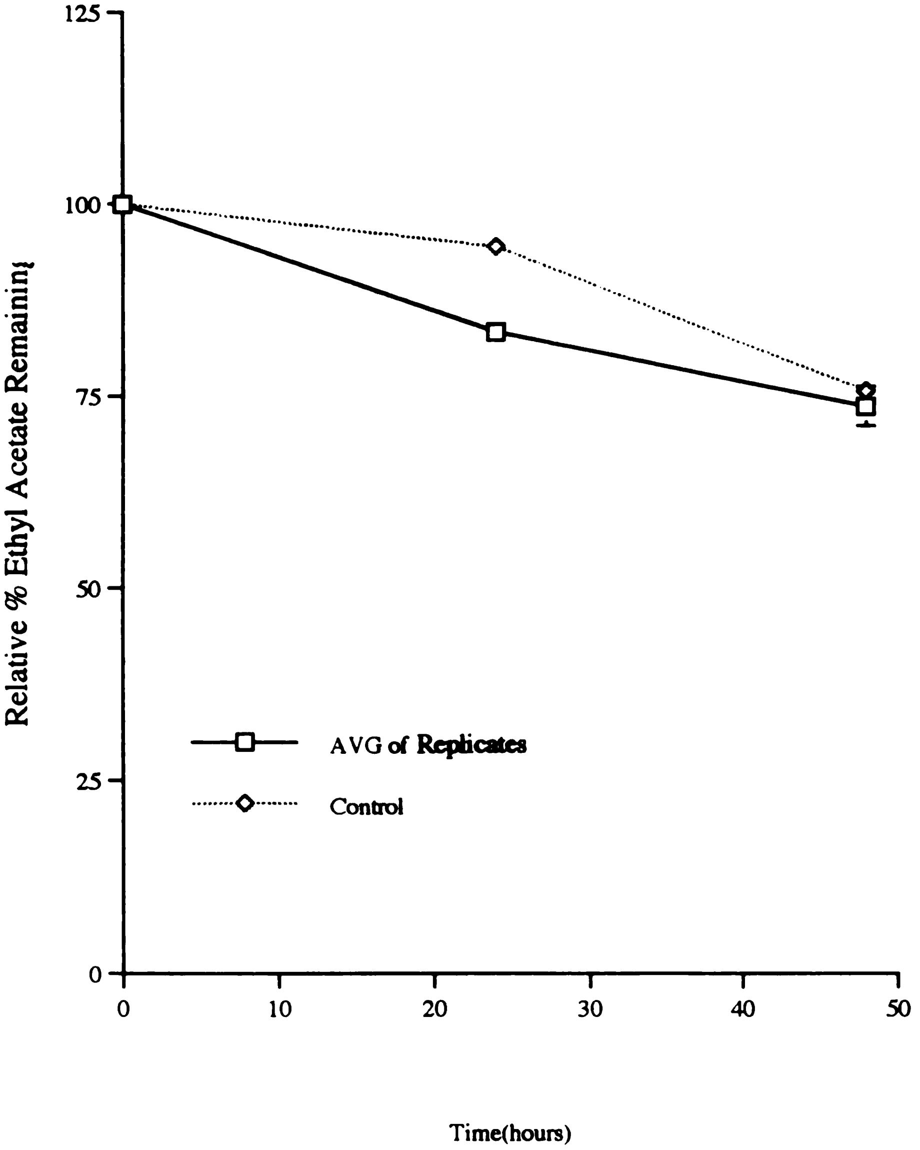


Figure 15. Sorption Capacity of Adcote 548 Adhesive for Ethyl Acetate

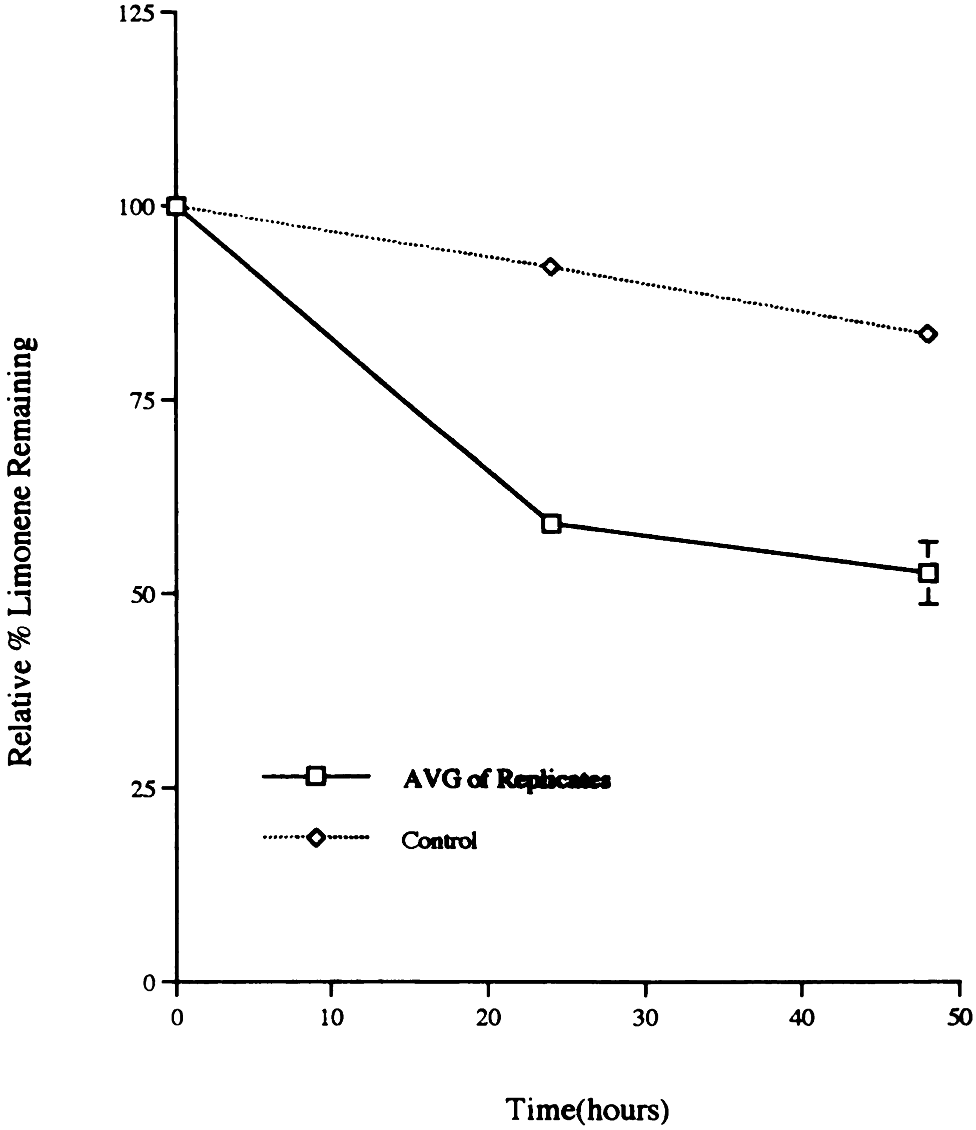


Figure 16. Sorption Capacity of Adcote 548 Adhesive for Limonene

4. Sorptive Capacity of the Adhesive Matrix Dispersed Sorbent Systems

Based on the findings of the sorption capacity of the adhesive layer for the respective sorbates, it was assumed that the Adcote adhesive would provide an acceptable matrix for evaluating the sorptive capacity of the adhesive matrix dispersed sorbent systems. In this case, the adhesive is the continuous phase and the sorbent is the dispersed or discontinuous phase. The results of the studies carried out to evaluate the sorptive capacity of a series of adhesive matrix dispersed sorbent system, for the test sorbate compounds, are summarized in Table 5 and presented graphically in Figures 17-19 . As shown in Table 5, the sorption of hexanal and ethyl acetate by the adhesive matrix dispersed sorbent systems was equivalent to that of the adhesive system alone, indicating that the sorbent / adhesive composites were ineffective in sorbing hexanal and ethyl acetate, although the non-matrix dispersed sorbents were quite effective in sorbing these respective sorbates. To determine the significance of the sorbent effects, the Dunnett's t-test was used to compare individual mean values with the control group (Gill, 1978). From Table 6, for hexanal, adhesive with aluminum oxide and adhesive with Amberlite XAD-4 showed significant differences at 99% confidence level, when compared to the control group after 48 hours. From Table 7, for ethyl acetate, adhesive with

Florisil (95% confidence level) and adhesive with Amberlite XAD-4 (99% confidence level) presented significant differences, when compared to the respective control group.

The ineffectiveness of the matrix dispersed sorbent system in sorbing hexanal and ethyl acetate, while not fully understood, may be attributed to:

(1). the slow rate of diffusion of the sorbate through the adhesive layer

(2). inactivation of the active sites of the sorbents as a result of the binding of residual solvent or interaction with the adhesive polymer functional groups

For limonene as the sorbate, Florisil and Amberlite XAD-4 dispersed within the adhesive matrix proved to be highly effective sorbent systems, while the other sorbent / adhesive composites were ineffective in sorbing limonene. The results of the sorption studies carried out with limonene and the adhesive matrix dispersed sorbent systems are presented graphically in Figure 19. From Table 8, for ethyl acetate, adhesive with Florisil and adhesive with Amberlite XAD-4 presented significant differences at the 99% confidence level, when compared to the control group.

Table 5. Sorption Capacity of Sorbents Impregnated Adhesive Layer

Storage Time (hours)	Sorb- bents Organics	Relative Percent Sorbate Remaining [a][b]						
		Silica Gel	Alumina	Florisil	Tenax	XAD-4	XAD-7	Control
0	Hexanal	100%	100%	100%	100%	100%	100%	100%
24		73.9%	79.0%	75.0%	69.3%	55.6%	69.7%	67.7%
48		61.7%	74.5%	57.0%	54.0%	31.8%	58.7%	57.7%
0	Ethyl Acetate	100%	100%	100%	100%	100%	100%	100%
24		82.9%	88.5%	81.1%	84.7%	77.5%	81.2%	83.4%
48		69.9%	80.2%	70.2%	73.8%	62.6%	74.6%	73.7%
0	Limonene	100%	100%	100%	100%	100%	100%	100%
24		54.8%	60.7%	64.7%	83.7%	53.3%	59.2%	59%
48		46.9%	46.6%	19.9%	59.1%	17.5%	32.1%	52.6%

(a) Storage temperature = 21 ± 1°C

(b) Average of triplicate analysis

Table 6: Statistics Comparison of Sorption of Adhesive Mixed with Sorbents Coated Film for **Hexanal**

Code	Treatment of Sorbents:
Ctrl	Adhesive coated film without sorbent (Control)
1	Adhesive with Silica Gel
2	Adhesive with Alumina Oxide
3	Adhesive with Florisil
4	Adhesive with Tenax
5	Adhesive with Amberlite XAD-4
6	Adhesive with Amberlite XAD-7

Time Effects:

0 hour injection
24 hours injection
48 hours injection

Comparison	Difference (t-value)[1]	
	24 hours	48 hours
1 vs Ctrl	1.53	0.97
2 vs Ctrl	3.11*	4.71**
3 vs Ctrl	1.89	0.66
4 vs Ctrl	0.12	1.58
5 vs Ctrl	4.06**	8.40**
6 vs Ctrl	0.26	0.15

---

1. Difference between the tabled Dunnett's t-value (two-sided) and the calculated t-value. * = significant at $P \leq 0.05$; ** = significant at $P \leq 0.01$.

$t_{D(\alpha=0.05, m=6, \nu=15)} = 2.89$
$t_{D(\alpha=0.01, m=6, \nu=15)} = 3.71$

Table 7: Statistics Comparison of Sorption of Adhesive Mixed with Sorbents Coated Film for **Ethyl Acetate**

Code	Treatment of Sorbents:
Ctrl	Adhesive coated film without sorbent (Control)
1	Adhesive with Silica Gel
2	Adhesive with Alumina Oxide
3	Adhesive with Florisil
4	Adhesive with Tenax
5	Adhesive with Amberlite XAD-4
6	Adhesive with Amberlite XAD-7

Time Effects:

0 hour injection
24 hours injection
48 hours injection

Comparison	Difference (t-value)[1]	
	24 hours	48 hours
1 vs Ctrl	0.57	2.84
2 vs Ctrl	2.49	2.70
3 vs Ctrl	1.54	3.08*
4 vs Ctrl	0.43	0.73
5 vs Ctrl	3.46*	6.78**
6 vs Ctrl	1.46	0.30

---

[1] Difference between the tabled Dunnett's t-value (two-sided) and the calculated t-value. * = significant at $P \leq 0.05$; ** = significant at $P \leq 0.01$.

$t_{D(\alpha=0.05, m=6, \nu=17)} = 2.85$
$t_{D(\alpha=0.01, m=6, \nu=17)} = 3.63$

Table 8: Statistics Comparison of Sorption of Adhesive Mixed with Sorbents Coated Film for **Limonene**

Code	Treatment of Sorbents:
Ctrl	Adhesive coated film without sorbent (Control)
1	Adhesive with Silica Gel
2	Adhesive with Alumina Oxide
3	Adhesive with Florisil
4	Adhesive with Tenax
5	Adhesive with Amberlite XAD-4
6	Adhesive with Amberlite XAD-7

Time Effects:

0 hour injection
24 hours injection
48 hours injection

Comparison	Difference (t-value)[1]	
	24 hours	48 hours
1 vs Ctrl	4.19**	4.60**
2 vs Ctrl	0.15	4.78**
3 vs Ctrl	3.09*	24.45**
4 vs Ctrl	17.06**	4.38**
5 vs Ctrl	6.69**	26.18**
6 vs Ctrl	0.96	15.44**

---

1. Difference between the tabled Dunnett's t-value (two-sided) and the calculated t-value. * = significant at $P \leq 0.05$; ** = significant at $P \leq 0.01$.

$t_{D(\alpha=0.05,m=6,v=17)} = 2.85$
$t_{D(\alpha=0.01,m=6,v=17)} = 3.63$

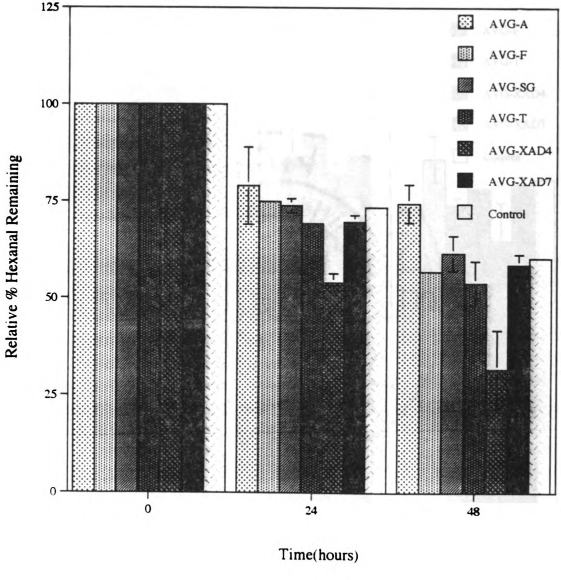


Figure 17. Sorption Capacity of Sorbent Impregnated Adhesive Layers for Hexanal (A : Aluminum Oxide, F : Florisil, SG : Silica Gel, T : Tenax, XAD-4 : Amberlite XAD-4, Amberlite XAD-7)

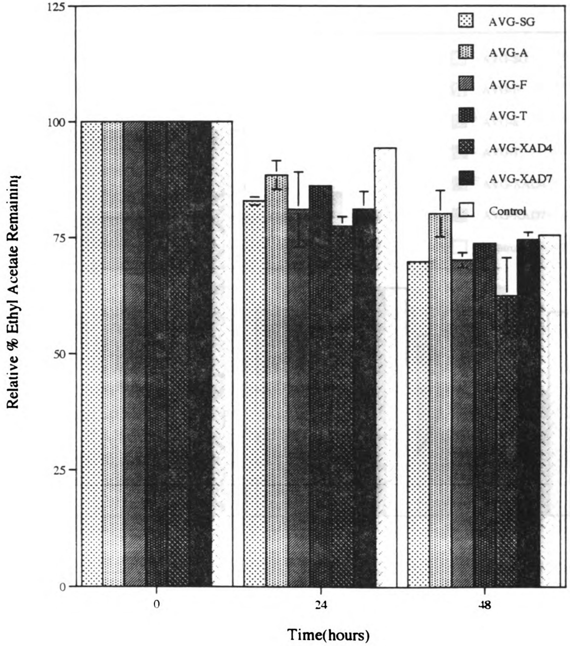


Figure 18. **Sorption Capacity of Sorbent Impregnated Adhesive Layers for Ethyl Acetate (A : Aluminum Oxide, F : Florisil, SG : Silica Gel, T : Tenax, XAD-4 : Amberlite XAD-4, Amberlite XAD-7)**

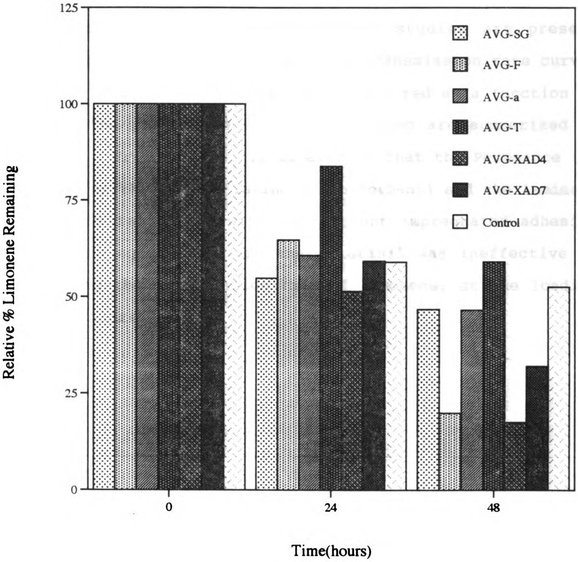


Figure 19. **Sorption Capacity of Sorbent Impregnated Adhesive Layers for Limonene (A : Aluminum Oxide, F : Florisil, SG : Silica Gel, T : Tenax, XAD-4 : Amberlite XAD-4, Amberlite XAD-7)**

5. Permeation

The results of the permeation studies are present graphically in Figure 20, where the transmission rate curves for the respective film samples are plotted as a function of time. The permeation values calculated are summerized in Table 9. From Table 9, it is evident that the Permeance (P) values for the control laminate (no sorbent) and the laminate structure fabricated with the sorbent impregnated adhesive layer are equivalent, and that Florisil was ineffective in modifying the transmission rate of limonene, at the loading level utilized.

Table 9. The Effect of Adhesive Matrix Dispersed Sorbent on the Permeation of Limonene through OPP / Adhesive / Saran

Film Sample (OPP/Adhesive/Saran-F)	Transmission Rate (μg/day)x10^{-4}	Permeance ($\mu g/m^2\cdot$day$\cdot$mmHg)
Florisil Impregnated Adhesive Layer	6.4±1.3(a)	1.1±0.2(a)
Control	6.6	1.1

(a) Average of replicate analysis

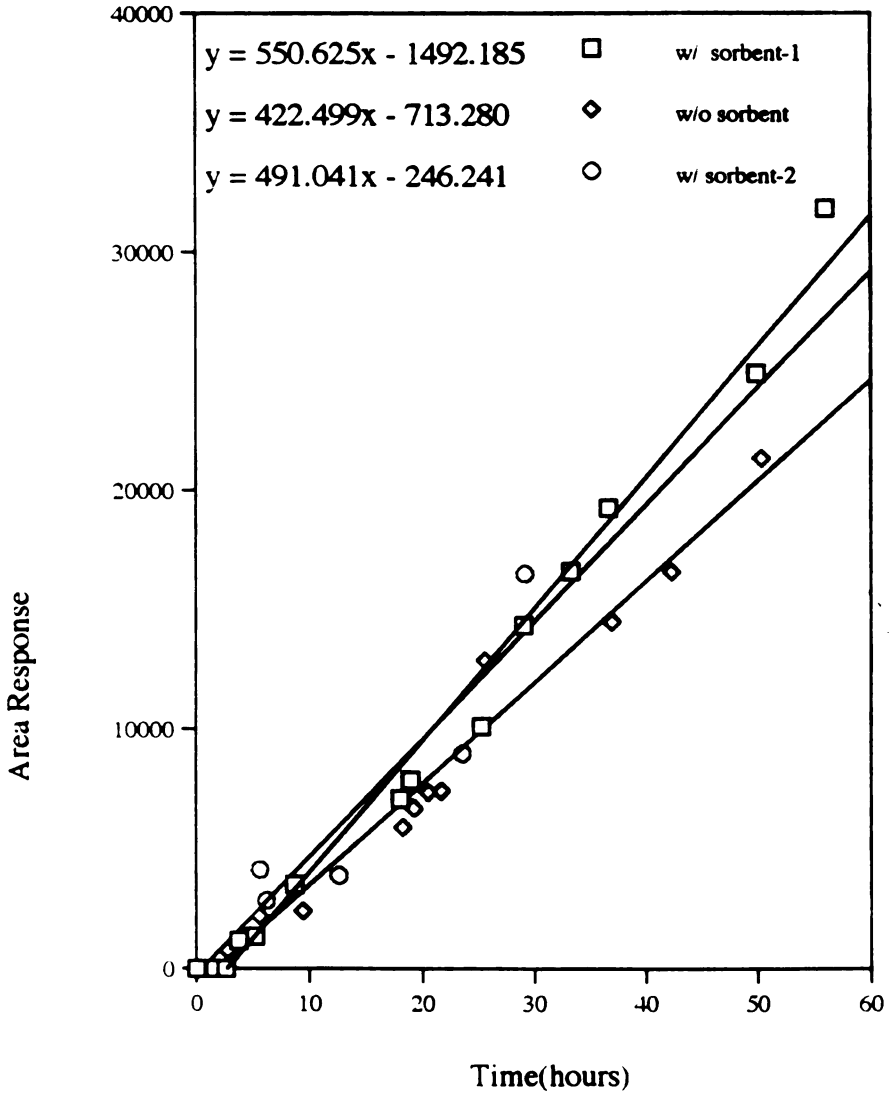


Figure 20. Comparison of Limonene Permeation Between Sorbent Impregnated and Non-sorbent Impregnated Film

SUMMARY AND CONCLUSION

- The seal integrities of three sorption cell systems, which included a 450 ml Pint jar system, a serum vial with Mininert valve system, and a sure/seal Oxford bottle system, were determined in this study. The sure/seal bottle was found to retain the highest levels of added sorbate. For example, the sure/seal bottle maintained 80% of the hexanal added, while the 450 ml Pint jar and serum vial with Mininert valve can only 20% of the hexanal added, after 48 hours storage at 23 °C.

- Studies carried out to evaluate the sorptive capacity of a series of sorbents showed that most sorbents tested were very effective in sorbing hexanal, ethyl acetate, and limonene. Amberlite XAD-4 and XAD-7 showed varying results, as regards specific sorbates.

- The sorption capacity of the cured adhesive (Adcote 548), which had been coated onto aluminum foil, was evaluated for the three selected sorbates. The results showed limited levels of sorption of the respective sorbates by the Adcote 548 adhesive system. It was assumed therefore that the Adcote 548 adhesive would provide an acceptable matrix for evaluating the sorptive capacity of the adhesive matrix dispersed sorbent systems, where the adhesive is the continuous phase and the sorbent is the dispersed or discontinuous phase.

- Florisil dispersed within the adhesive matrix showed high sorption capacity for limonene.
- The permeability of limonene through a polypropylene based laminate structure to which Florisil had been incorporated into the adhesive layer, showed that the Florisil was ineffective in modifying the transmission rate of limonene at the loading level.

POSSIBLE FUTURE STUDIES

Based on the results obtained in the present study, a number of additional area of investigation can be proposed. Some potential future areas of study are as follows:

- Consider utilizing a sorbent of smaller particle size. This would result in a significant increase in the surface area of the sorbent, which should result in an increase in sorption capacity per unit mass of sorbent.
- Use of a sorbent of smaller particle size could also provide a means of increasing the loading level of the sorbent, and still provide a uniform dispersion within the adhesive matrix.
- Consider other adhesive system, such as a water based adhesive or a 100% solids adhesive. Selective of a water based adhesive would limit sorbents to types which would not sorb water.
- Consider incorporating the sorbent directly into to polymer layer of a coextrusion type lamination. For example, incorporate a sorbent into a regrind type layer in a coextrusion.

APPENDICES

APPENDIX I

APPENDIX I

Table 10. Hexanal Calibration Data

Density of Hexanal = 0.834 g/cc

Calibration Factor = 8.93 x 10^{-14} g/AU

Concentration (ppm,v/v)	Total Quantity Injected ($x10^{-9}$g)	Area Response
1	0.834	8737
5	4.170	38631
10	8.340	65227
20	16.680	176945
40	33.360	365870

Table 11. Ethyl Acetate Calibration Data

Density of Ethyl Acetate = 0.893 g/cc

Calibration Factor = 3.26 x 10^{-13} g/AU

Concentration (ppm,v/v)	Total Quantity Injected ($x10^{-9}$g)	Area Response
1	0.893	3052
5	4.465	17436
10	8.930	29147
20	17.860	55088
40	35.720	111570

Table 12. Limonene Calibration Data

Density of Limonene = 0.840 g/cc

Calibration Factor = 4.53×10^{-14} g/AU

Concentration (ppm,v/v)	Total Quantity Injected ($\times 10^{-9}$g)	Area Response
1	0.84	32036
5	4.20	108542
10	8.40	218228
20	16.80	412512
40	33.60	754600

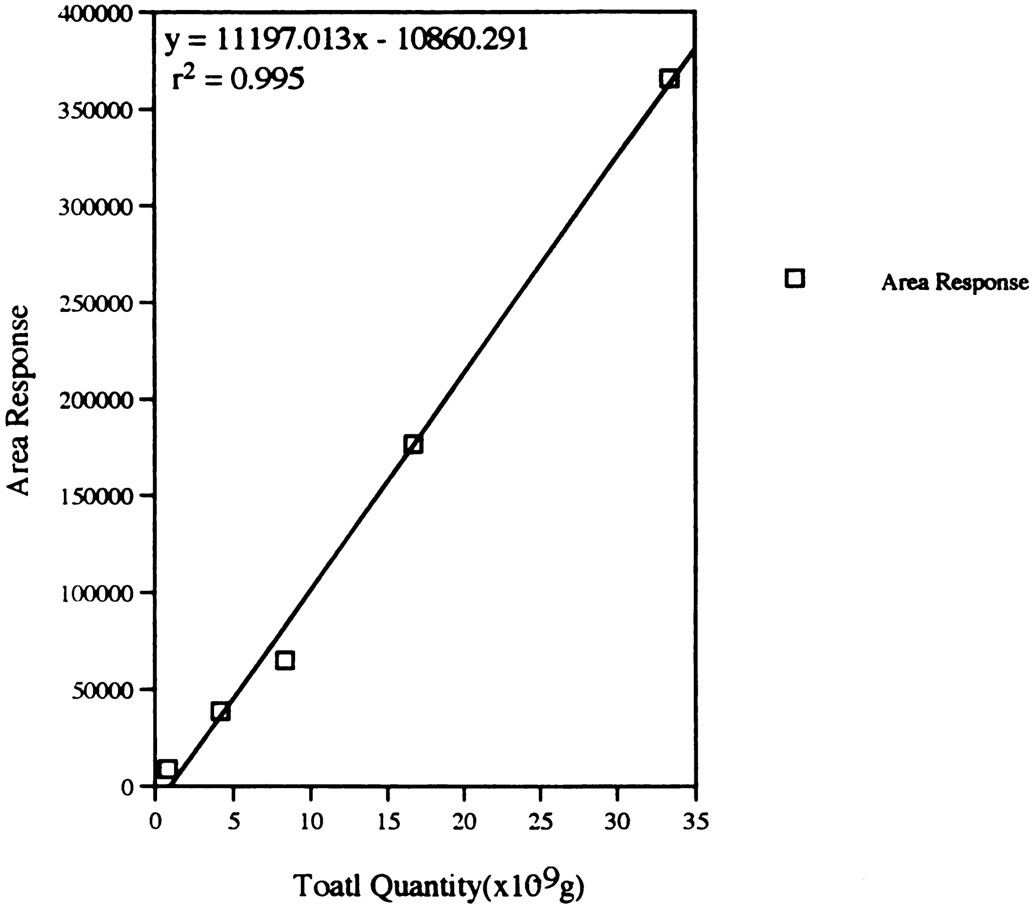


Figure 21. Standard Calibration Curve for Hexanal

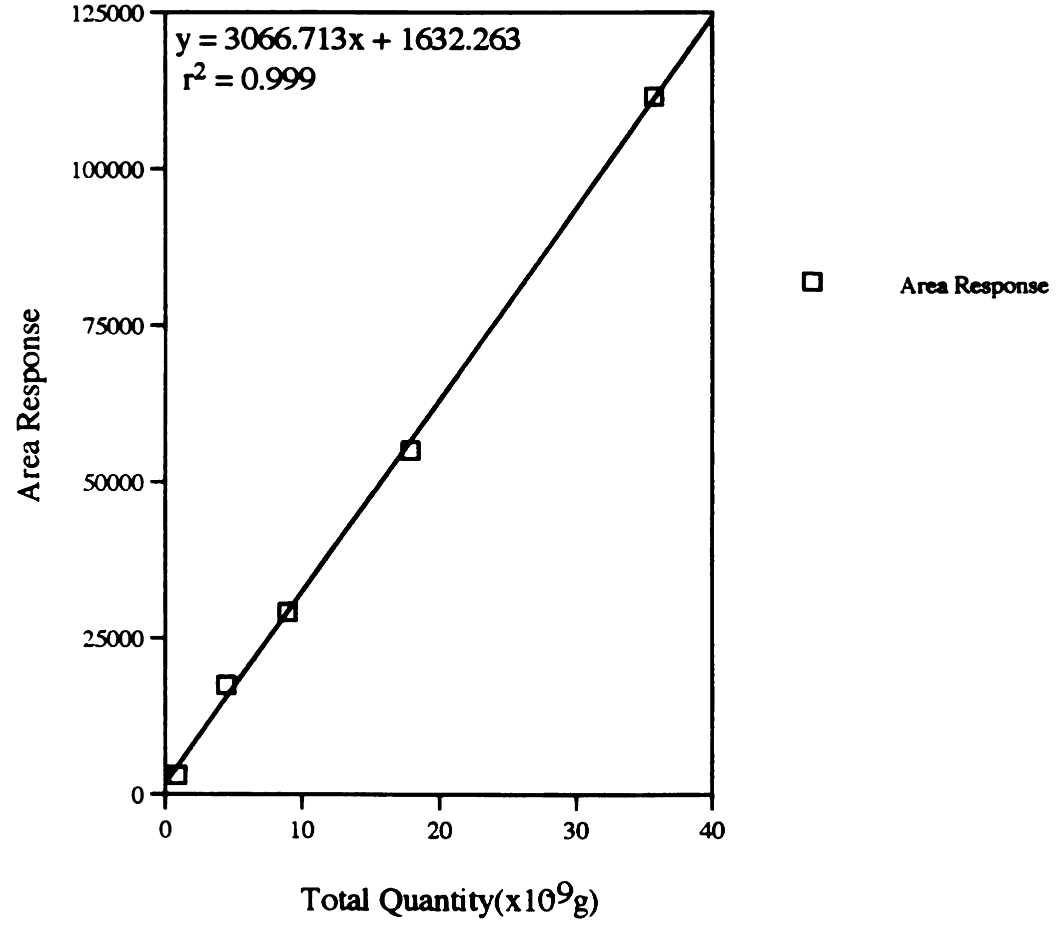


Figure 22. Standard Calibration Curve for Ethyl Acetate

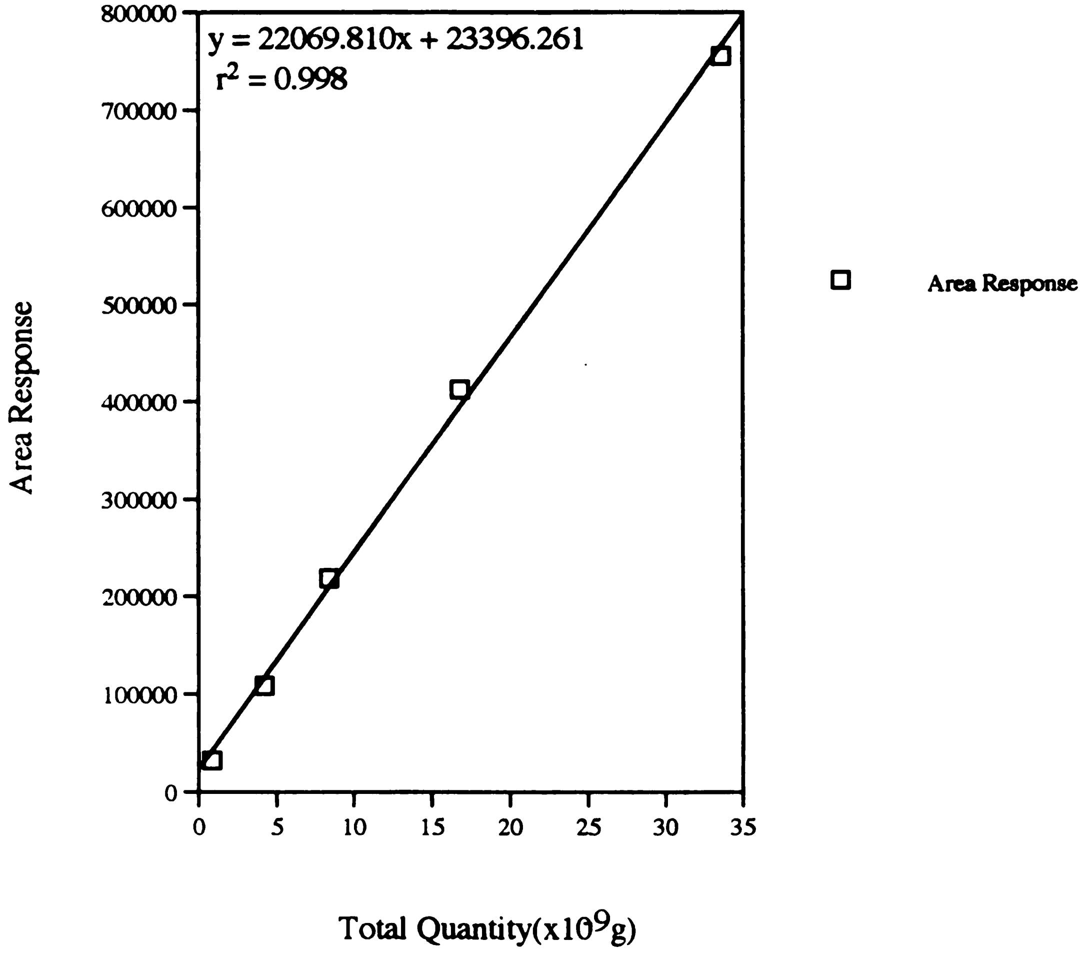
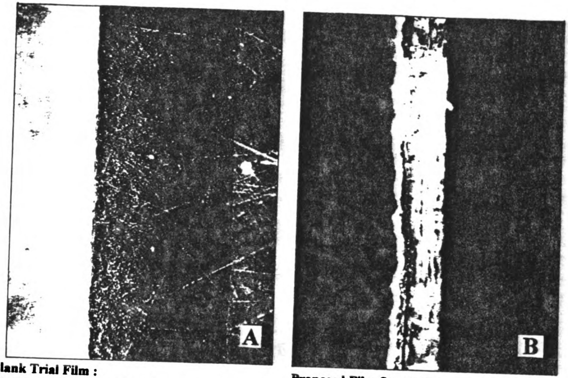


Figure 23. Standard Calibration Curve for Limonene

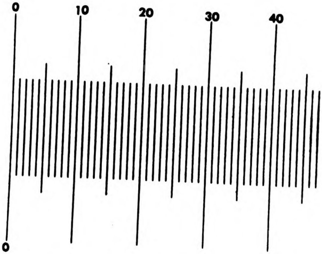
APPENDIX II

Figure 24. Micrographs from Optical Microscope



Blank Trial Film :
Aluminum Foil/Absorbent Impregnated Adhesive

Proposed Film Structure :
OPP/Absorbent Impregnated Adhesive/Saran®



One Smallest Scale = 0.01 mm

APPENDIX III

APPENDIX III

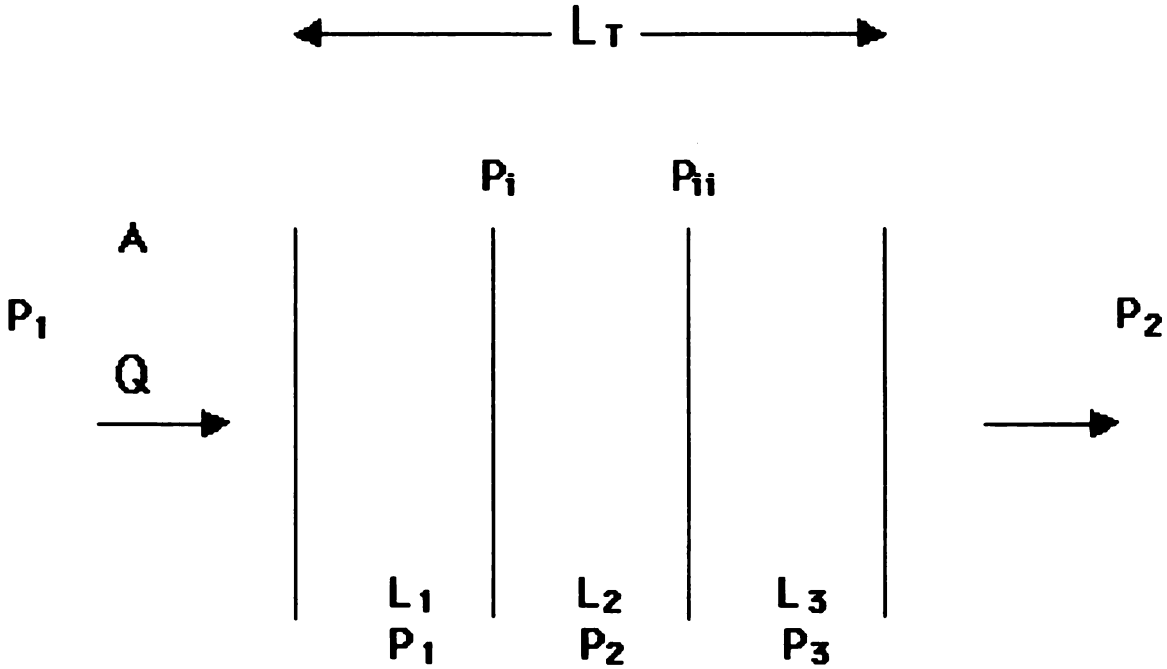


Figure 25. Estimating the Permeation for Multilayer Structure

$\Delta P = P1 - P2$

$\Delta P1 = Pi - P1$

$\Delta P2 = Pii - Pi$

$\Delta P3 = P2 - Pii$

$\Delta P = \Delta P1 \neq \Delta P2 + \Delta P3$

$$P_T = \frac{Q \times L_T}{A \times \theta \times \Delta P} \qquad \Delta P = \frac{Q \times L_T}{A \times \theta \times P_T}.$$

$$P_1 = \frac{Q \times L_1}{A \times \theta \times \Delta P_1} \qquad \Delta P1 = \frac{Q \times L_1}{A \times \theta \times P_1}.$$

$$P_2 = \frac{Q \times L_2}{A \times \theta \times \Delta P_2} \qquad \Delta P2 = \frac{Q \times L_2}{A \times \theta \times P_2}.$$

$$P_3 = \frac{Q \times L_3}{A \times \theta \times \Delta P_3} \qquad \Delta P3 = \frac{Q \times L_3}{A \times \theta \times P_3}.$$

APPENDIX IV

APPENDIX IV

Cell Seal Integrity:

Different Sorption cell Systems:

1. 450 ml Pint Jar/Closure system
2. Serum Vial with Mininert Valve System
3. Sure/Seal Oxford Bottle with Crown Cap

Time Effects:

0 hour injection
24 hours injection
48 hours injection

Table 13: Analysis of Variance for Sealing Integrity

Source	df	SS	MS	F
Total	26	30681.23		
Replication	2	33.17	16.58	0.35
Jar	2	8482.55	4241.27	88.41**
Error (a)	4	191.89	47.97	
Time	2	16493.73	8246.86	130.13**
Jar x Time	4	4719.40	1179.85	18.62**
Error (b)	12	760.50	63.38	

Coefficient of variation: 11.90 %

Sorbent Sorption for Three Organics:

Treatment of Sorbents:

Control: without sorbent
1. Silica Gel
2. Alumina Oxide
3. Florisil
4. Tenax
5. Amberlite XAD-4
6. Amberlite XAD-7

Time Effects:

0 hour injection
24 hours injection
48 hours injection

Table 14: Analysis of Variance for Sorbent Sorption of Hexanal

Source	df	Hexanal	Ethyl Acetate	Limonene
			Mean Square	
Replication	1	5.65*	0.17	0.01
Sorbents	6	2961.69**	3754.03**	2948.37**
Error (a)	6	3.40	8.65	4.10
Time	2	33008.14**	23760.29**	30701.66**
Sorbent x Time	12	56.30**	965.21**	813.54**
Error (b)	14	1.30	2.86	3.15
Coefficient of variation (%)		2.59	3.22	3.85

Sorption of Adhesive Mixed with Sorbents Coated Film:

Treatment of Sorbents:

Control: Adhesive coated film without sorbent
1. Adhesive with Silica Gel
2. Adhesive with Alumina Oxide
3. Adhesive with Florisil
4. Adhesive with Tenax
5. Adhesive with Amberlite XAD-4
6. Adhesive with Amberlite XAD-7

Time Effects:

0 hour injection
24 hours injection
48 hours injection

Table 15: Analysis of Variance for Sorption of Adhesive mixed with Sorbents Coated Film

Source	df	Hexanal	Ethyl Acetate	Limonene
			Mean Square	
Replication	1	17.49**	0.004	4.21*
Sorbents	6	265.37**	50.73**	370.63**
Error (a)	6	26.85	15.40	4.22
Time	2	6881.29**	2729.81**	13161.50**
Sorbent x Time	12	85.81**	16.73**	89.72**
Error (b)	14	10.50	7.63	2.04
Coefficient of variation (%)		4.29	3.25	2.13

Comparisons treatments with control groups (Gill, 1978):

The judgment of significance is to detect the adhesive impregnated with selected absorbents have better sorption of flavor than adhesive without sorbent for sorbates. The calculated Dunnett's t-value is compared with two-sided Dunnett's t-tabulated data.

For each of the m=t-1 comparisons with the control, compute the sample variance of the difference between the mean at hand (i) and the control (c).

$$t = (\bar{y}_i - \bar{y}_c) / \sqrt{2\hat{\sigma}^2 / 3}$$

The approximate number for degree of freedom:

$$\hat{\sigma}^2 = (MS_{E1} + 2MS_{E2}) / 3$$

$$\hat{\upsilon} = \left[\hat{\sigma}^2\right]^2 / \left\{ \frac{(MS_{E1}/3)^2}{6} + \frac{(2MS_{E2}/3)^2}{14} \right\}$$

Dunnett's t table value (Gill, 1978):

$$t_{D,0.05,m=6,\hat{\upsilon}} = t_{D,0.05,m=6,15.1} = \pm 2.89$$

$$t_{D,0.01,m=6,\hat{\upsilon}} = t_{D,0.01,m=6,15.1} = \pm 3.71$$

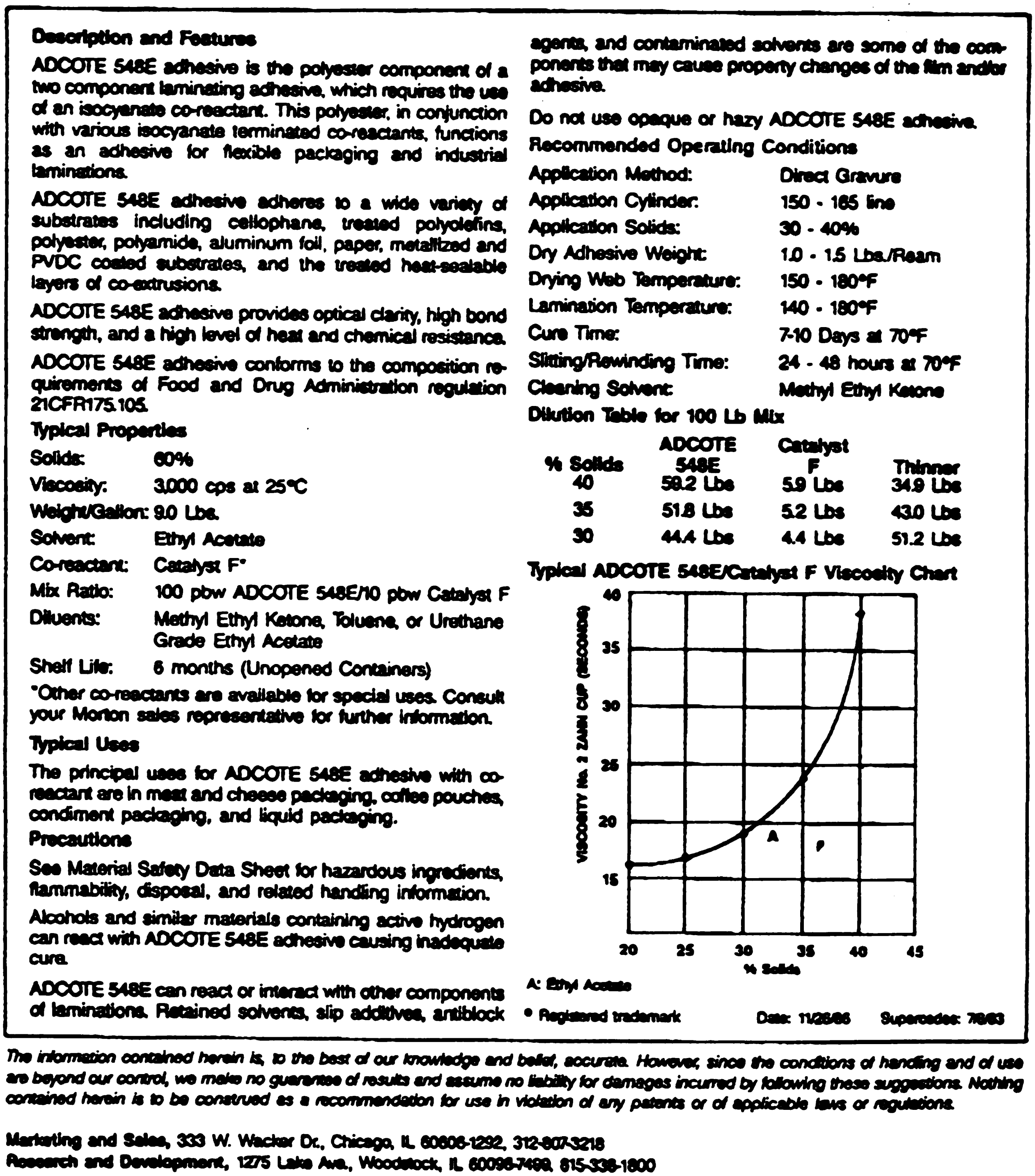
$$t_{D,0.05,m=6,\hat{\upsilon}} = t_{D,0.05,m=6,16.7} = \pm 2.86$$

$$t_{D,0.01,m=6,\hat{\upsilon}} = t_{D,0.01,m=6,16.7} = \pm 3.65$$

APPENDIX V

APPENDIX V

Adhesives and Coatings - ADCOTE 548E Adhesive (Morton Thiokol Inc.)



Description and Features

ADCOTE 548E adhesive is the polyester component of a two component laminating adhesive, which requires the use of an isocyanate co-reactant. This polyester, in conjunction with various isocyanate terminated co-reactants, functions as an adhesive for flexible packaging and industrial laminations.

ADCOTE 548E adhesive adheres to a wide variety of substrates including cellophane, treated polyolefins, polyester, polyamide, aluminum foil, paper, metallized and PVDC coated substrates, and the treated heat-sealable layers of co-extrusions.

ADCOTE 548E adhesive provides optical clarity, high bond strength, and a high level of heat and chemical resistance.

ADCOTE 548E adhesive conforms to the composition requirements of Food and Drug Administration regulation 21CFR175.105.

Typical Properties

Solids:	60%
Viscosity:	3,000 cps at 25°C
Weight/Gallon:	9.0 Lbs.
Solvent:	Ethyl Acetate
Co-reactant:	Catalyst F*
Mix Ratio:	100 pbw ADCOTE 548E/10 pbw Catalyst F
Diluents:	Methyl Ethyl Ketone, Toluene, or Urethane Grade Ethyl Acetate
Shelf Life:	6 months (Unopened Containers)

*Other co-reactants are available for special uses. Consult your Morton sales representative for further information.

Typical Uses

The principal uses for ADCOTE 548E adhesive with co-reactant are in meat and cheese packaging, coffee pouches, condiment packaging, and liquid packaging.

Precautions

See Material Safety Data Sheet for hazardous ingredients, flammability, disposal, and related handling information.

Alcohols and similar materials containing active hydrogen can react with ADCOTE 548E adhesive causing inadequate cure.

ADCOTE 548E can react or interact with other components of laminations. Retained solvents, slip additives, antiblock agents, and contaminated solvents are some of the components that may cause property changes of the film and/or adhesive.

Do not use opaque or hazy ADCOTE 548E adhesive.

Recommended Operating Conditions

Application Method:	Direct Gravure
Application Cylinder:	150 - 165 line
Application Solids:	30 - 40%
Dry Adhesive Weight:	1.0 - 1.5 Lbs./Ream
Drying Web Temperature:	150 - 180°F
Lamination Temperature:	140 - 180°F
Cure Time:	7-10 Days at 70°F
Slitting/Rewinding Time:	24 - 48 hours at 70°F
Cleaning Solvent:	Methyl Ethyl Ketone

Dilution Table for 100 Lb Mix

% Solids	ADCOTE 548E	Catalyst F	Thinner
40	58.2 Lbs	5.9 Lbs	34.9 Lbs
35	51.8 Lbs	5.2 Lbs	43.0 Lbs
30	44.4 Lbs	4.4 Lbs	51.2 Lbs

Typical ADCOTE 548E/Catalyst F Viscosity Chart

A: Ethyl Acetate

• Registered trademark

Date: 11/26/86 Supersedes: 7/8/83

The information contained herein is, to the best of our knowledge and belief, accurate. However, since the conditions of handling and of use are beyond our control, we make no guarantee of results and assume no liability for damages incurred by following these suggestions. Nothing contained herein is to be construed as a recommendation for use in violation of any patents or of applicable laws or regulations.

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