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Development of a Test Method to Determine the Relative Barrier Performance of Polymeric Films to Flavor Loss of Methyl Salicylate

By

Russell J. Wright

A Thesis

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M. S. DEGREE THESIS

The M. S. Degree thesis of Russell J. Wright
has been examined and approved
by the thesis committee as satisfactory
for the thesis requirements for the
Master of Science Degree.

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July 30, 1998

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ABSTRACT

The increased use of polymer films to package a wide range of flavor compounds in various products creates a problem in trying to recommend appropriate materials. There is a need to identify tools that enable the engineer to simplify the selection process through ranking the relative adsorption of such compounds with different polymer films.

The study of one such compound, Methyl Salicylate, was conducted for polymer films representing commodity and engineering barrier films. The films tested were Polypropylene, Polyethylene Terephthalate, Polyethylene Napthalate, Aclar, and Liquid Crystal Polymer. The testing was conducted with a Thermogravimetric Analyzer to determine the relative amount of penetrant adsorbed by each film; thereby enabling a ranking of expected barrier performance. The results indicate that the Liquid Crystal Polymer (LCP) film sample had the lowest rate of adsorption of Methyl Salicylate. Further studies are recommended to refine the method and evaluate multiple flavor adsorption behaviors.

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Chapter I

Introduction

A. Problem Statement

The rate of adsorption and permeation of flavor compounds varies with the product and polymer film contact surface. Current film selection methods do not avoid costly over packaging, nor do they deliver optimum product quality and shelf life.

B. Hypothesis

A test method can be developed to determine the relative barrier performance of various polymeric films to flavor loss.

C. Package Development Needs

The business needs of the global community of today require the package to deliver a high quality product regardless of the distribution system employed. The marketing needs for innovation, shelf impact and speed to market require the packaging engineer to deliver customized materials that are engineered to meet these objectives. These factors are added to the challenge of sorting through the vast array of new and improved flexible materials and coatings available for developing an appropriate package. The objective of this research project is to develop an experimental technique for use in ranking the barrier performance to flavor adsorption by various polymeric films. The leading candidates can then be evaluated for machineability, price and formal shelf life testing, thereby making effective use of research time and cost by eliminating ineffective candidates from long term studies. The specific flavor used for this evaluation is methyl salicylate, however the techniques are applicable to most flavor compounds. The traditional model of identifying a supplier with whom an engineer can develop a functional package is no longer relevant. The recommended method is a more proactive involvement with material science specialists at the raw material level, in an effort to design barrier needs into their new product development programs, that satisfy your product's requirements. The technology partnerships that are created will enhance performance and innovation needs for your packaging.

Over the past few years, flexible packaging has grown at a faster rate than any other packaging forms. Today flexible packaging is estimated to be a $16 billion business, employing a total of 375,000 people in the United States of which 84,000 are employed directly according to the Flexible Packaging Association (Burns,1997). Several factors contributing to overall market growth are:

- the substitution of specialized packaging that includes enhanced barriers for traditional consumer product packaging.
- Continued concerns over solid waste and resource reduction.
- Steady growth in the use of stand-up pouches.
- Rapid growth in the low-fat, no-fat food categories which require increased moisture barriers.
- Continued growth in the institutional packaging sector.
- Increased penetration into the medical and pharmaceutical packaging markets.

These trends and needs are dictating growth in mass customization which can be facilitated by development of strategic technology partnerships and simplified test methods for delivering required barrier characteristics.

The efforts to customize flexible materials requires a discussion of the basic process by which flavor loss occurs. The mechanism for loss of flavor consists of three major steps:

- Adsorption and solubility of penetrant into the polymer.
- Diffusion of the penetrant through the polymer.
- Desorption and evaporation of the penetrant from the surface of the polymer.

The challenge is to approach the gas barrier level of metal or glass. The property of plastics to adsorb and extract organic compounds commonly refered to as ‘scalping’, adds to the difficulty in identifying an appropriate film. The objective is to develop a realistic and convenient analytical method to evaluate differences in aroma absorbing potential of various flexible, packaging materials (Baner,1991). A determination of the relative quantity sorbed will help select a packaging material that delivers a stable flavor/aroma profile. The other concern relative to flavor sorption is its affect on package integrity, which could result in delamination or other physical failure (Arora,1991).

Chapter II

Literature Review

A. Polymer Basics

Consumer goods flexible packaging was revolutionized in the 1920s by the commercialization of cellophane.

For the first time, the buyer could see the contents of the package through a film that protected the packaged items from dirt, moisture, and atmospheric gases (Osborn,1992). The growth of cellophane continued through the early 1950s, when high polymers were commercialized with better properties at a lower cost. By the 1980s, plastic films had replaced 90% of the cellophane use in flexible packages.

The plastics industry continues to be an aggressively growing business consisting of a wide range of applied polymer science markets. Polymeric materials range from structural adhesives, protective coatings, manmade fibers, reinforced composites to molded and extruded plastics used in packaging.

A simple plastic is created when a large number of identical repeating units are joined together to make a very large molecule or polymer (from the Greek polys meaning many, and meros, meaning parts). The mer is the smallest repetitive unit in a polymer (Bakker,1986).

The starting unit in the growth of the polymer chain is a combination of elemental carbon, hydrogen, oxygen, nitrogen and halogens, which forms the mer. The monomer is taken through the polymerization sequence of initiation, propagation and termination to grow the polymer in a coordinated fashion based on its intended application. The chain length is a critical component in determining the usefulness of the macromolecule formed. The degree of polymerization (DP) is an indication of the number of links or repeating units in the chain. The length of a linear polymer chain is usually described by its molecular weight, which is the molecular weight of the monomer multiplied by the number of monomers in the chain.

The definition of a polymer consists of three parts, the material must be:

1. organic....containing carbon
2. high molecular weight....25,000+
3. plastic....able to change shape during the manufacturing process

All three are necessary to define a polymer (Driscoll,1997).

There are several schemes used to classify a resin, the most important is as thermosetting(TS) or thermoplastic(TP). This classification indicates whether the material can be remelted. Plastics that can be recycled and reused are thermoplastics. An example of a thermoplastic-type process is water freezing into ice that can be repeatedly reformed with no loss in properties. An example of thermosetting-type process is hard-boiling an egg. The egg undergoes a chemical and physical change that is irreversible. Thermoplastics make-up more than two-thirds of all polymers used today (Bakker,1986). There are two general types of materials within the general category of thermoplastics, as distinguished by the methods of formation from monomers. Addition polymers are usually formed by continuous reaction of an unsaturated carbon-carbon bond monomer, e.g., ethylene, to the active end of a pre-existing polymer chain (see table 1).

Table 1 - Chemical Structure of Vinyl-type Thermoplastics

Common Name	R1	R2	R3	R4
Polyethylene	H	H	H	H
Polypropylene	H	H	CH3	CH3
Polyvinylchloride	H	H	H	Cl
Polytetrafluorethy-lene	F	F	F	F
Polystyrene	H	H	H	C6H5
Polyvinylalcohol	H	H	H	OH
Polyvinylacetate	H	H	H	OCCH3 O
Polyacrylonitrile	H	H	H	CN

(Bakker,1986)

Condensation polymers are usually produced by reaction of one or two (or more) saturated monomers with reactive end groups, i.e., hydroxyl, carboxyl, amine. The polymerization reaction is characterized as an equilibrium reaction (Wiley. Polymers are grouped for convenience in two economic groups: commodity polymers and engineering polymers. Only a few of the available polymers are of practical significance for packaging purposes. These are all in the commodity thermoplastic grouping (Soroka,1995).

Properties, such as toughness, stiffness, transparency and barrier to gases are imparted by the chemical nature of the units making up the polymer.

Several other classification schemes used to describe polymers include:

1) Molecular composition - halogens, oxygen...

2) Chemical grouping - aliphatic (-CH_2-) and aromatic (C_6H_6)

3) Polymer architecture or morphology - molecular weight (MW), molecular weight distribution (MWD), and branching

4) Chain structure - four broad categories:

- linear - long chains

- branched - long backbone with pendant side chains

- cross-linked - linear chains connected by short, low molecular weight groups, forming a 3-dimensional network

- ladder - highly developed growth of multi-unit rings, tightly connected

5) Homogeneity - a homopolymer (polyethylene) based on one starting monomer; a copolymer (impact polystyrene) based on two starting materials; terpolymer (acrylonitrile-butadiene-styrene) based on three starting co-monomers.

The high development cost and time involved to develop new polymers has introduced a trend of creating polymeric alloys or blends based on existing polymers with predictable and profitable processability.

6) Crystallinity - a key polymer attribute that ranges from amorphous (no crystallinity) to increasing crystalline content (degree of crystallinity). Typically physical properties improve with crystallinity at the expense of processability.

7) Chemical formation - two major subdivisions based on how reactants combine and if a by-product is produced:

a) Polycondensation - A + B = Poly C + by-product

examples: thermoplastic polyesters(PET) and polyamides (nylons)

b) Polyaddition - monomer A polymerized to Polymer A with no by-product

examples: members of the olefin, vinyl, and styrenic families

9) Polymer performance - typically a marketing approach to characterization based on criteria that includes: the number

of manufacturers, volume produced, selling price, and func-

tional properties offered (see table 2).

a) Commodity - first generation polymers produced by many suppliers, sell in billions of pounds, cost $.25 -$.75 per pound, and offer marginal performance.

b) Transitional - plastics with a broad performance and price range and overlap into both commodity and engineering classification, sell in 500 million+ lb. range, cost $.75 - $1.25.

c) Engineering - second generation polymers produced by few companies, sell in hundreds of millions of pounds, priced from $1.25 - $3 per pound, and offer enhanced functional performance.

c) Performance - next generation polymers, typically one supplier, up to several million pounds, priced upwards to $20 per pound or more, and provide outstanding functional properties.

Table 2 -Classification of Thermoplastic Polymers

Commodity	Transitional	Engineering	Performance
Polyethylene	ABS/SAN	Nylon(6 & 66)	Fluoropolymer
Polypropylene	SMA copolymer	PBT	Liquid Crystal Polymers
Polystyrene	Acrylics	Polyacetal	Polyarylate
Polyvinyl-chloride		Polycarbonate	Polyimide
PET		Alloys & blends	Polysulfone
			Polyamideimide

(Muccio,p107)

“There are more than 20 principal classes of polymers today, with new subclasses being created by ingenious combinations of polymers, additives, fillers, etc. Development of desired properties for a specific packaging application depends upon a good understanding of comparative molecular architecture of candidate polymers" (Bakker,1986). Several of the attributes that influence the properties of polymers are:

1) Molecular weight - the molecular weight of the repeat unit multiplied by the number of times the monomer is repeated, then add the end-group molecular weights; low molecular weight yields easier processing, while high molecular weight gives better properties

2) Crystallinity - degree of order within a polymer, ranges from non-crystalline or amorphous (PVC,PS) to highly crystalline (polyolefins, PET)

3) Glass transition temperature - the temperature at which a polymeric material changes from a solid state to a soft, rubbery state

4) Orientation - the alignment of polymer chains through processing stress to enhance barrier and other properties

5) Molecular attractions - strong covalent bonds join atoms together in polymers, while inter molecular or Van der Waals forces yield varying degrees of polarity. The polarity influences many material properties. Polymer selection for various applications should follow the principal that 'like dissolves like' in regards to polarity.

A basic understanding of polymers is an invaluable tool to facilitating the material selection process, however the advances in processing, coating, and lamination technology add even more accuracy to the packaging selection process, as discussed in the section that follows on polymer films.

B. Technology of Polymer films

The process for making films transforms solid polymer resin in granular or pellet form into films on rolls. The first part of this transformation is the extrusion sequence, which consists of the following steps:

Polymer feed ⇒ Melting ⇒ Mixing ⇒ Metering ⇒ Filtration

All extruded polymers must go through the complete sequence, and variations in each step to accommodate differences in polymer characteristics are relatively subtle.

The second part, the film making sequence, consists of the following steps:

Melt Film Formation ⇒ Quenching ⇒ Orientation ⇒ Windup

The orientation step may or may not be used depending on the polymer (Park,1973).

The plastic films typically used in the packaging industry are made by either the cast film process or the tubular or blown film process. The cast film process feeds the melt through a flat die to a cold metal roll or into a water bath for quenching or rapid cooling. The blown film process forms a molten tube, blown like a bubble to generate a large diameter tube from a small circular die. Typically cooling is accomplished through an air cooling ring. The formed tube is then collapsed and can be slit into two sheets for windup.

Blown films tend to be more crystalline due to their relatively long cooling period, and have a higher haze level than cast films. The more efficient quenching of cast film results in a higher throughput for thicker films. Nevertheless there are benefits of higher crystallinity for blown films, such as greater stiffness and improved barrier to moisture and gases. Similarly, cast film quenched on a roll is slightly better in these properties than water-quenched film (Park,1973).

Film orientation in the cast and blown film processes offer some variation in the level of crystallinity. Orientation induces higher levels of crystallinity, which enhance barrier and optical properties. The flat film orientation process consists of the following steps:

Melt Film Formation ⇒ Melt Film Quenching ⇒ Film Reheating ⇒ Film Stretching(through the use of a tenter frame) ⇒ Film Heat Setting

The tubular orientation process consists of the following steps:

Melt Film Formation ⇒ Melt Film Quenching(aided by a water bath) ⇒ Film Reheating ⇒ Film Stretching ⇒ Film Heat Setting

Typically cast and blown film processes are part of the vertical integration of many larger film converters. Oriented film processes with higher capital investment and technical complexity are operated by larger companies with experience in making plastic films.

Plastic films produced by any of the aforementioned processes often do not have the necessary properties for the demands of typical packaging applications. Secondary processing is often accomplished by converters. The key criteria for film conversion is surface adhesion, which can be accomplished through flame treatment, corona treatment or priming of the surface.

“Various processes to incorporate plastics into flexible packaging are advancing, including extrusion coatings, liquid-based coatings, and film laminations. New polymerization technologies are offering a wider range of potential properties, and the incorporation of additives and/or compounds allow resin suppliers and film producers and converters to further modify base polymer properties” (Strupinsky,1997).

There are two types of coating systems: dispersion, where the coating polymer is dispersed in water with a surfactant and solvent, where the coating polymer is dissolved in a solvent. In both systems, the liquid medium is evaporated once the coating is applied leaving behind a film coating(Park,1973). Solvent coatings often leave behind a residue that can add unwanted taste and odor to packaged products. “The extrusion coating process resembles the cast film process, which uses a roll to quench the film” (Park,1973). Extrusion coating is used extensively in coating foil and paper. Plastic films are typically coextruded in the film forming process to take advantage of the economies. However, for thicker coatings this secondary process is employed. Film lamination broadens the properties of a wide range of coated and uncoated films and relies on strong adhesive bonds between films. A combination of these techniques is employed to deliver cost effective flexible films with tailored barrier and mechanical properties for today's demanding packaging applications. The selection of the polymers for each layer establishes the properties of the film, since the properties are a combination of those contributed by each layer. The most recent trend in film forming technology of micro-thin layer coextrusion reinforces the principle of barrier contribution by each layer. The most recent development of a commercial, nine layer, blown coextruded film in Australia leads this technology trend.

C. Sorption Theory

The growing trend of an increased usage of polymeric packaging requires a better understanding of the physical/chemical interaction of products and packages. Polymer properties for small molecules such as: oxygen, water, and carbon dioxide are well known. However, there is a need for a more comprehensive understanding of the mechanisms by which organic molecular mass transfer occurs in polymeric packaging materials (Delassus,1994).

The phenomenon occurs in several steps: adsorption, absorption, diffusion, and desorption. The first step, adsorption is described as the preferential partitioning of organic compounds onto the surface of the polymeric material. Adsorption is driven primarily by concentration of the product and the package surface, a surface to volume ratio. Once the organic is adsorbed, absorption, a process in which material penetrates the polymer to form a solution occurs. The solution process is followed by penetrant molecular diffusion through the polymer by a series of random hops. The diffusion process is followed by penetrant molecular desorption from the low pressure side of the polymeric material. This process is called permeability (P) and is useful in describing the rate of mass transport through a polymer at steady state. Equation 1 is a restatement of Fick's First Law of diffusion in terms familiar to packaging individuals.

$$\Delta Mx / \Delta t = (P\ A\ \Delta px) / L \qquad (1)$$

Where $\Delta Mx / \Delta t$ is the rate that material X permeates a polymer film with a cross sectional area A and thickness L when a difference in partial pressure of the permeant Δpx , exists across the film. It is applicable for small molecules, such as oxygen and water, and for larger flavor/aroma/solvent (F/A/S) molecules (Delassus,1994).

Equation 2 shows how P is related to two more basic properties.

$$P = D \times S \qquad (2)$$

Where D is the diffusion coefficient, a kinetic term that describes how fast molecules move in a polymer host. S is the solubility coefficient, a thermodynamic term that describes how many molecules dissolve in a polymer host (Delassus,1994). The reader is referred to Crank(1975) and Stastna(1995) for a thorough mathematical treatment of molecular transport and sorption.

Several factors affect sorption, diffusion and permeation in polymers:

1. Size and shape - an increase in penetrant size normally results in a decrease in the diffusion coefficient value (D), and an increase in the solubility coefficient value (S). Since the permeability coefficient (P) is the product of these two parameters, its variation with penetrant size is much less.

2. Molecular branching - increasing branching causes a decrease in diffusivity.

3. Chemical composition - penetrant diffusion and permeability are generally higher when the polymer and penetrant are of similar chemical composition or polarity (like dissolves like).

4. Co-permeants - can affect the diffusion process by acting to plasticize the polymer matrix. May also result in competition for sites.

5. Morphology

The degree of crystallinity is significant, not only because crystalline regions are excluded from the sorption process but also because such regions are impermeable barriers to diffusion.

Cross linking by restraining mobility can decrease permeability, primarily by its influence on diffusion. A similar effect is achieved through polymer orientation.

6. Intermolecular forces - an increase in cohesive energy of a polymer normally causes polymer permeation to decrease.

7. Plasticizers and additives - plasticizers tend to force polymer chains apart thereby increasing the free volume of the system. Additives such as fillers can create a more torturous path for diffusion.

8. Temperature - as temperatures increase above Tg greater molecular motion occurs. This can lead to an increase in the size and frequency of hole formation, thus increasing permeability and diffusion (Barr,1997).

An important result of studies conducted by Baner, 1991 is the fact that barrier layers that are separated from direct product contact by a sealant layer have little influence on flavor sorption. The controlling influence is the sealant layer in contact with the product. Thus, improvements in material selection with regard to flavor sorption should be made by selecting sealing layers with minimal interaction with the product. (Baner,1991)

D. Organic Vapor Permeation Measurement Techniques

A variety of test methods are available to measure permeation of organic vapors in polymeric materials. The basic principle employed is similar, where a test film is mounted in a hermetic environment between two test cell chambers; the permeant to be tested is isolate on one side of the test film and then detected on the other side as a function of time. Using this data, the transmission rate and the permeability coefficient can be calculated. The four most common techniques are:

1. Absolute pressure method - the procedure and equipment are described under ASTM (American Society for Testing Materials) D-1434. This uses a pressure differential method that is essentially constant.

2. Gravimetric technique - measures the permeating gas by weight gain or loss through the use of an adsorbent filled polymer pouch or a TGA (thermogravimetric analyzer).

3. Isotactic method - the procedure and equipment are described under ASTM F1769-97. The method allows for continuous monitoring of the transmission rate of organic vapors through the test films from the initial time zero until steady state conditions. Two commercial instruments are available for permeation measurement. One is the Aromotran® (Modern Controls Inc., Minneapolis, MN) and the other is the MAS 2000 (MAS Technologies, Inc. Zumbrota, MN)

4. Quasi-isotactic method - a modification of the isotactic method, where the low concentration chamber of permeation cells is initially filled with carrier gas and completely closed. The permeated vapor is accumulated in the low concentration chamber by gas chromotography.

Additionally other methods include sorption - desorption techniques and analytical methods, such as distillation/extraction, direct (static) headspace, and dynamic headspace (or purge and trap) techniques.(Chang,1996)

Chapter III

Test Materials and Methods

A. Test Materials

The permeant selected for this study was Methyl Salicylate, a commonly used flavor oil. The sample was supplied by Rhone-Poulenc, Inc. located in Cranbury, NJ. The lot number is 81865 and the material specification number is MS400A015.

The test material sample range was selected to cover commodity resin films and the latest engineering resin films, promoted as high aroma barriers.

1. PEN ICI's Kaladex® the trademarked name for their biaxially oriented polyethylene napthalate (PEN) films. Targeted performance is between PET and polyimides. Samples provided by Active Industries, Inc. Willowbrook, IL.

thickness - .004 in.

2. CTFE - Allied Signal's Aclar® Rx 160 trademarked name for their chlorotrifluoroethylene (CTFE) homopolymer barrier film. Samples provided by Allied Signal Advanced Material, Pottsville, PA.

thickness - .0006 in.

3. PET - Dupont's Melinex® D888 trademarked name for their polyester barrier film. Samples provided by Dupont Polyester Films.

thickness - 48 gauge

4. PET - Dupont's Melinex® D888 trademarked name for their polyester barrier film. Samples provided by Dupont Polyester Films.

thickness - 76 gauge

5. LCP - Superex's Vectra® A-950 (Ticona is the supplier of the LCP pellets) trademarked name for their liquid crystal polymer barrier film. Samples provided by Superex Polymer, Inc.

thickness - .005 in.

6. OPP - Mobil's Bicor 150 ASB-X, two-side coated, sealable oriented polypropylene film. Samples provided by Mobil Chemical Co., Schaumburg,IL.

thickness - 1.5 mil

B. Test Method

Gravimetric studies were carried out with a TGA-7 Analyzer (Perkin Elmer), connected to a TAC7/DX Thermalanalysis Controller (Perkin Elmer). Thermogravimetric Analysis was used to determine the weight loss of polymer film samples that were conditioned by immersion in Methyl Salicylate. The weight loss of each sample represents the amount of Methyl Salicylate adsorbed by the film sample. The test procedure consisted of the following steps:

- 1 inch squares were cut from polymer film sheets.

- The squares were immersed in 10ml of Methyl Salicylate in a closed jar and stored at 40° C and 60% RH for 24 hours, and then held for 16 days at ambient conditions.

- The samples were removed from the jar and blotted dry.

- Each 1 in. sample was die cut with a .218 in. punch to fit the TGA pan.

- The polymer sample was placed in the tarred TGA pan and the initial weight was taken.

- The programmed heating cycle for the TGA was ramping at 20° C/minute from 30 - 250°C. Heating ran isothermally for 1 minute, then cooling was initiated.

- The percentage weight loss was measured from time zero temperature of 25° C to termination temperature of 250°C. The percentage weight loss, indicated as Delta Y, was used as the measure of adsorbance of Methyl Salicylate.

Chapter IV

Results and Discussion

The primary purpose of this study was to develop a simplified method for evaluating the relative adsorbance characteristics of Methyl Salicylate for six polymeric films. The intent was to provide the packaging engineer with a means to determine, qualitatively, which materials are best suited to provide the necessary aroma barrier in developing a flexible package. Table 3 summarizes the test results. The Delta Y values are an average of the tests conducted. The full set of data charts taken from material test runs, indicating percentage weight loss vs. temperature, are shown in the Appendix.

Table 3 – Thermogravimetric Data

Polymer Film	**Delta Y**
Liquid Crystal Polymer	.126
Polyethylene Napthalate	.257
Polyethylene Terephthalate (48gauge)	.791
Polyethylene Terephthalate (76gauge)	.813
Aclar	.912
Polypropylene	1.601

The data is directional in material selection for use with Methyl Salicylate containing products. The decision for further package development analysis and testing can be initiated using this data. Further testing must consider the human factor of detectable change in flavor or aroma, as well as, the physical requirements of the intended package application. The variation noted between multiple samples of the same material point to the need for continued method development, to include various temperature ranges and pre-conditioning. The TGA analysis does enable the packaging engineer to make qualitative recommendations for material selection, in a timely and cost effective manner. The highest barrier to adsorption appears to be provided by LCP, which is one of the newest entries in the high barrier, flexible film arena. The second best performance was noted as PEN a high barrier film and resin. The high cost of both of these materials limits their use to thin gauges in multilayer films requiring high barrier performance.

The commodity polymer PET was evaluated in two gauges to observe the affect an increased volume of polymer has on absorption. The higher Delta Y indicated for the thicker material reinforces the need for thinner product contact materials as the preferred barrier. The Aclar sample while a superior moisture barrier, appears to be less desirable in organic vapor barrier applications. The PP sample performed significantly worse than all other materials. Typically polyolefins offer negligible protection from flavor loss, however they are ideal sealant layer materials. Studies to minimize scalping through the use of thinner sealant layers, coatings and modified materials (metallocenes), can result in significant performance improvement in a final flexible package structure.

Chapter V

Summary and Conclusions

A gravimetric test method that utilized the Hewlett Packard Thermogravimetric Analyzer was developed to determine the relative adsorption of Methyl Salicylate by various polymeric films. The method was validated across six different film samples, each exhibiting a charecteristic percentage weight loss for the Methyl Salicylate adsorbed. This method offers the packaging engineer an efficient screening tool to select appropriate barrier materials for use when flavor /aroma loss are critical to product quality and shelf life.

The results listed in the previous section allow one to conclude the following:

1. The preferred barrier materials would be either PEN or LCP in packages used to store Methyl Salicylate containing products.

2. When selecting barrier materials minimizing the film thickness will reduce the amount of organic vapor absorbed.

3. On the basis of the results, the TGA method was found to be a suitable tool for use in qualifying relative performance of various barrier films to absorption of an organic vapor.

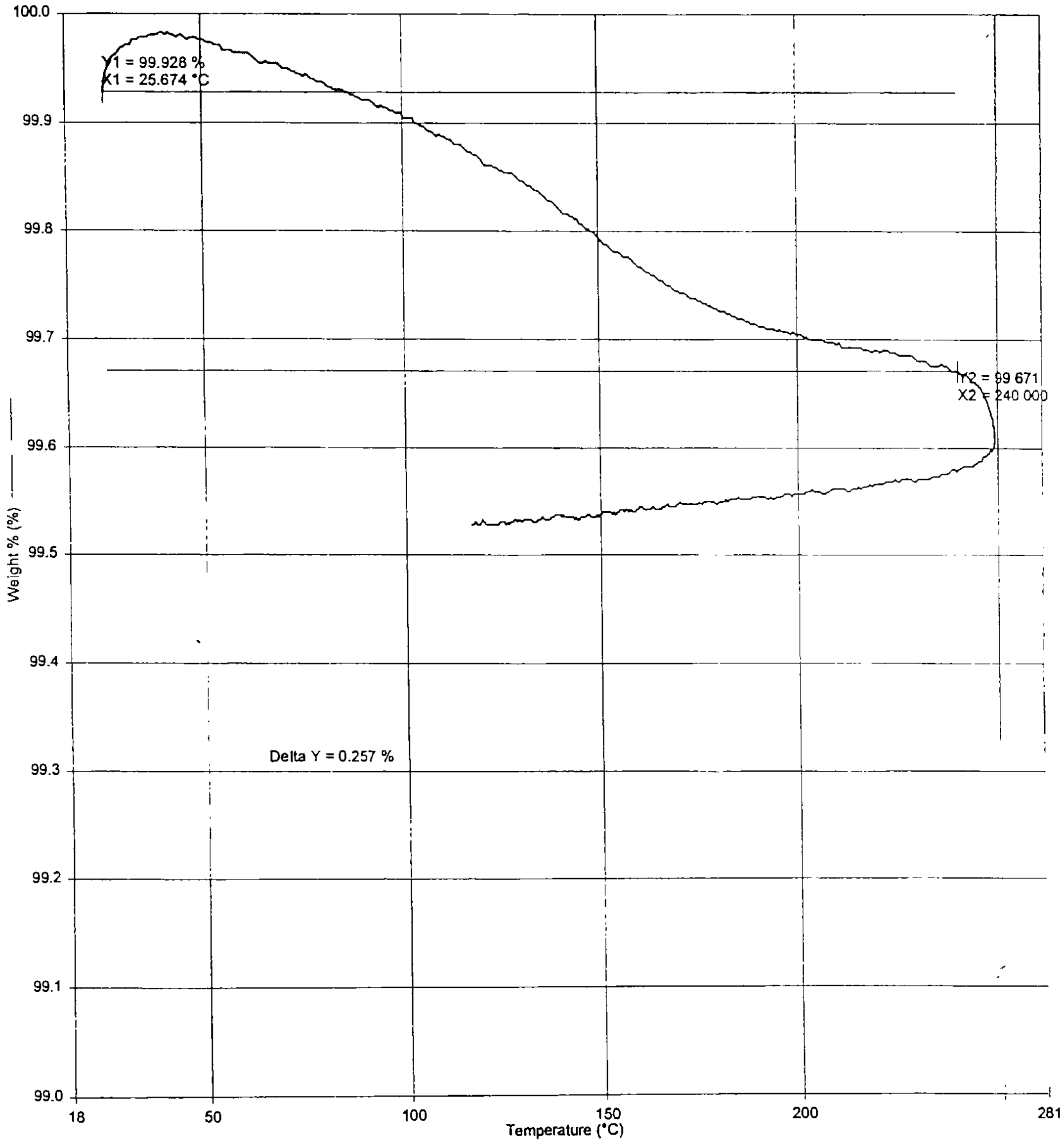
4. The Hypothesis that a test method can be developed to determine relative barrier performance of various polymeric films to flavor loss, is true.

Recommendation for Future Studies

This study indicates a relative performance of various barrier polymers with a single organic vapor. However, since most products contain multiple flavor compounds future studies should include multiple flavors to further validate the test method. Modification to the test method should be used to explore the TGA method's applicability to detect relative performance of surface coating technologies, which continue to be refined.

APPENDIX

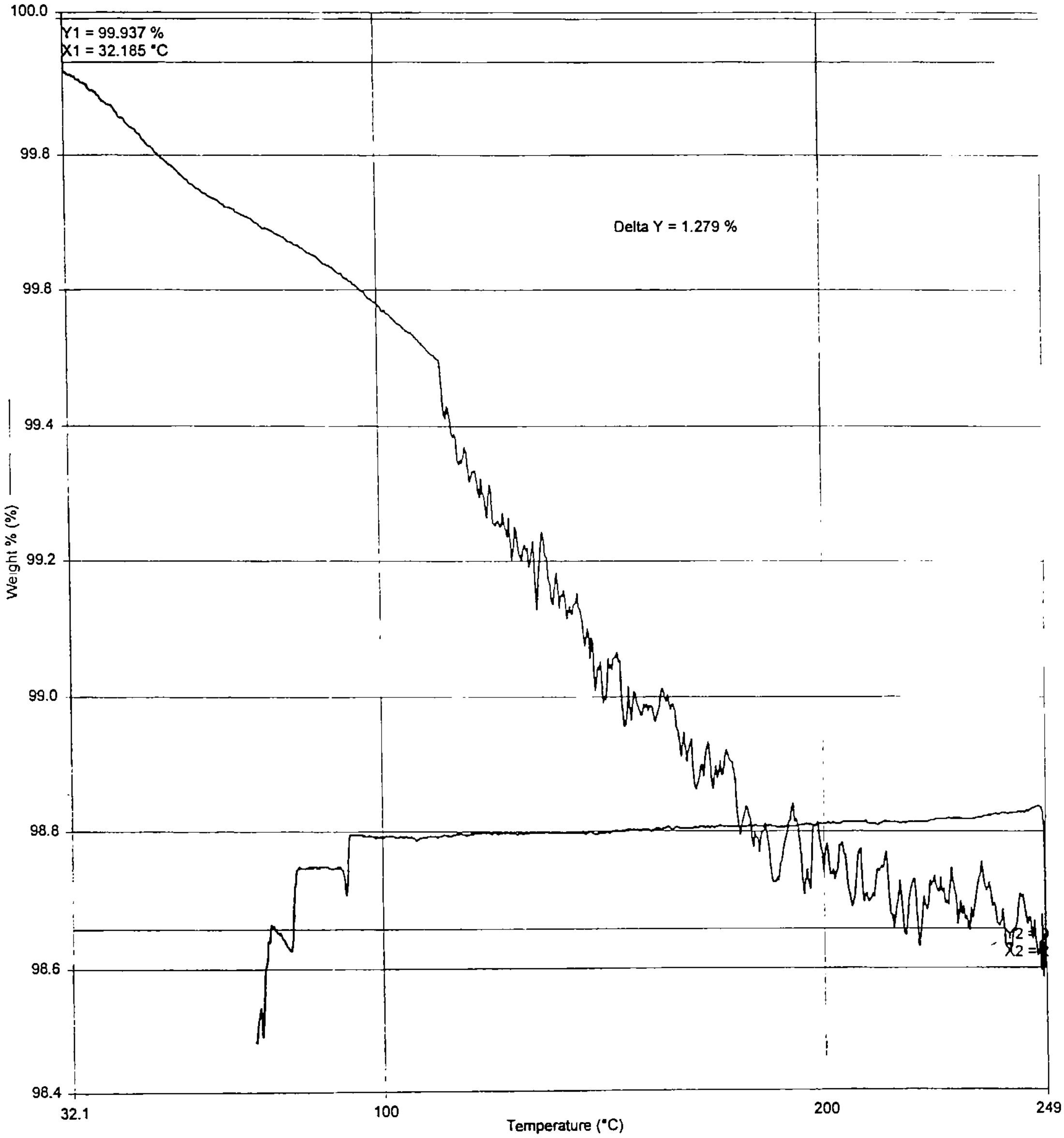
Filename: C:\PE\Pyris\...\QSAVE@980618160539.TGD
Operator ID: rjw
Sample ID: test A 2-Kaladex .004 " (PEN)
Sample Weight: 6.736 mg
Comment: Active Industries -ICI PEN
MP - 262 C / TG - 120 C



1) Heat from 30.00°C to 250.00°C at 40.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 40.00°C/min

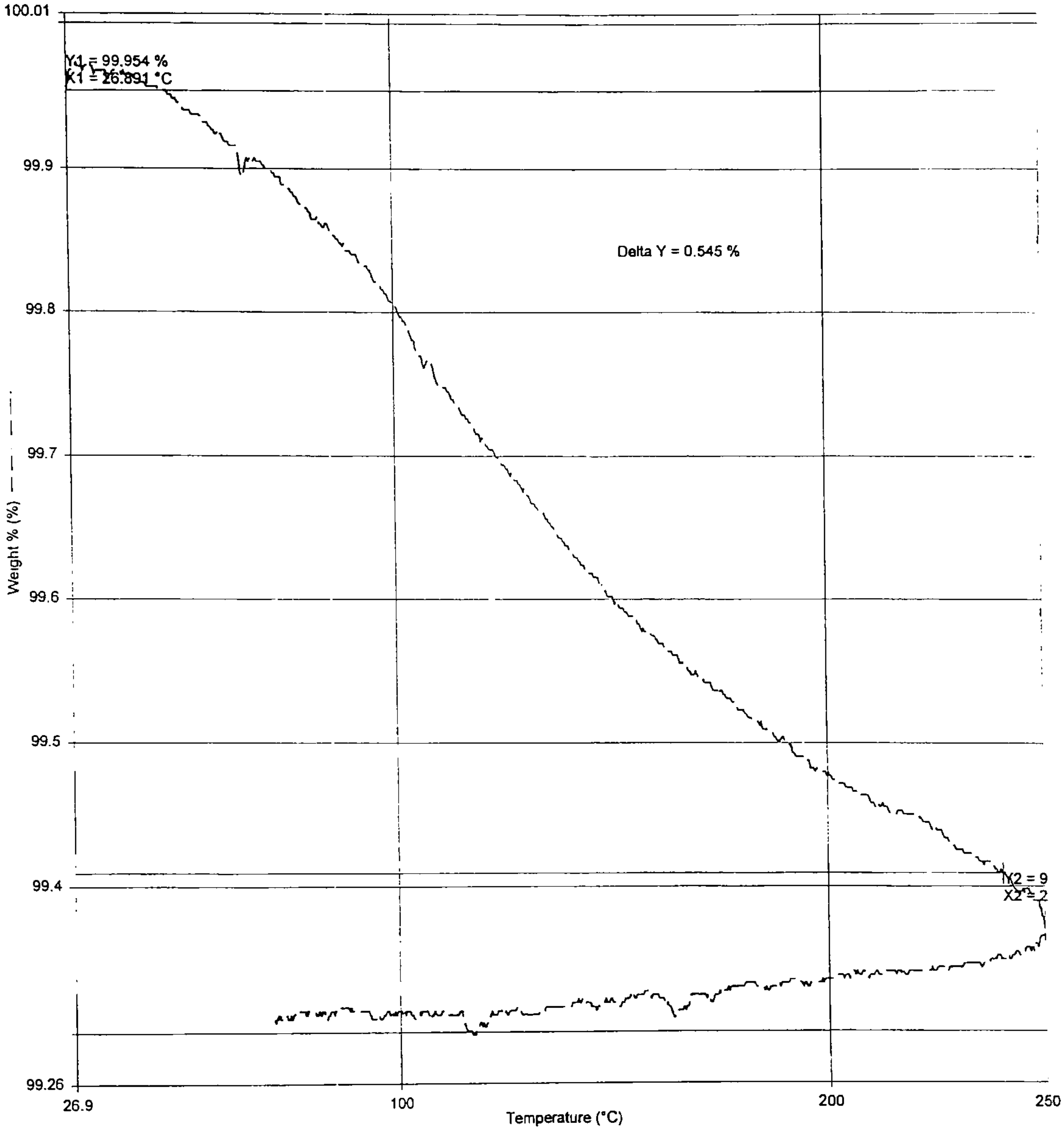
6/24/98 12:32:11 PM

Filename: C:\PE\Pyris\..\QSAVE@980618185423.TGD
Operator ID: rjw
Sample ID: test B 1 - Aclar Rx 160 .60 mil
Sample Weight: 8.874 mg
Comment: Allied Signal - Aclar
MP - 211 C



1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min
6/24/98 12:34:39 PM

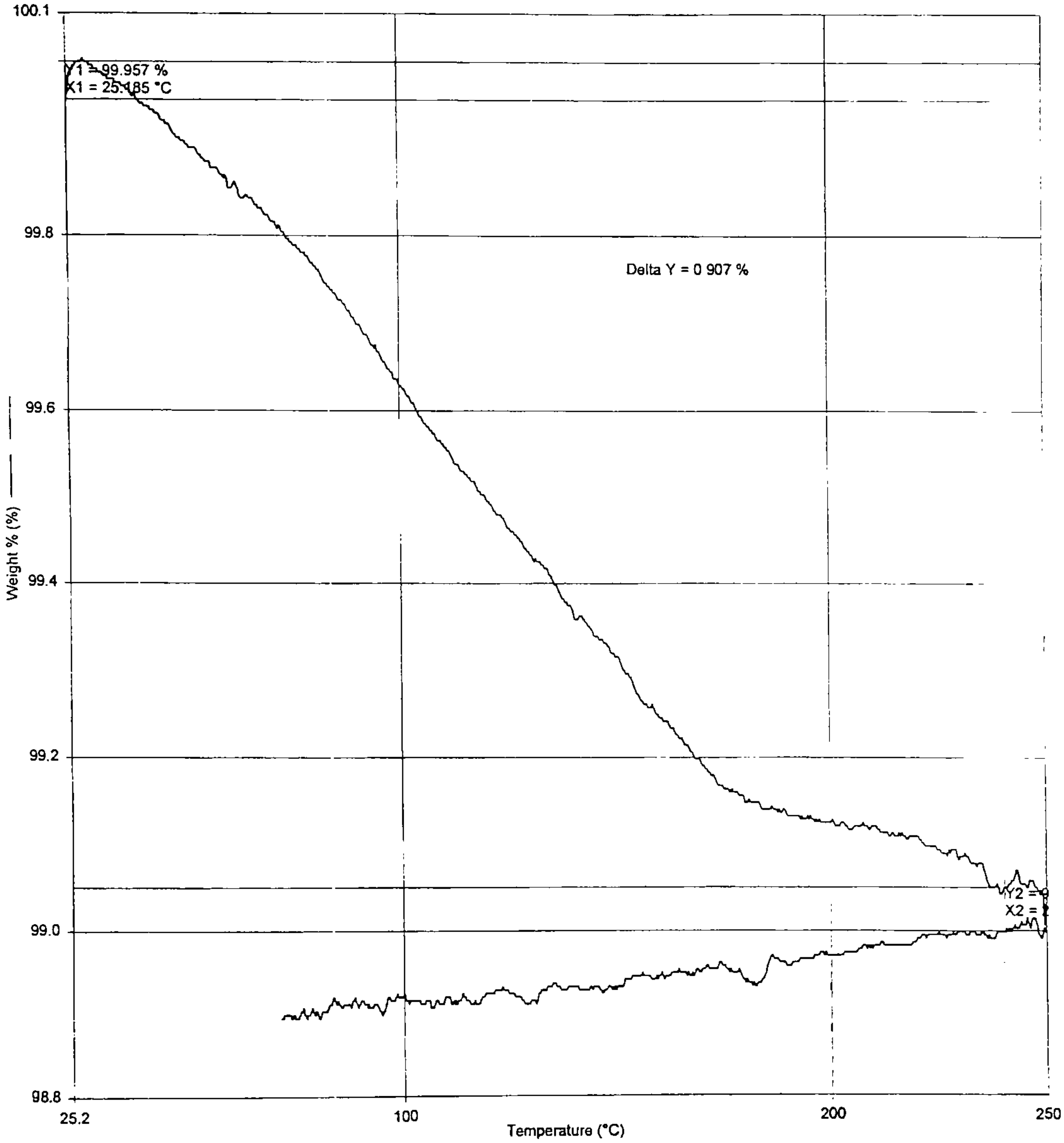
Filename:	C:\PE\Pyris\..\QSAVE@980619090954.TGD
Operator ID:	rjw
Sample ID:	test B 2 - Aclar Rx 160 .60 mil
Sample Weight:	5.925 mg
Comment:	Allied Signal - Aclar MP - 211 C



1) Heat from 30.00°C to 250.00°C at 20.00°C/min 2) Hold for 1.0 min at 250.00°C	3) Cool from 250.00°C to 30.00°C at 20.00°C/min

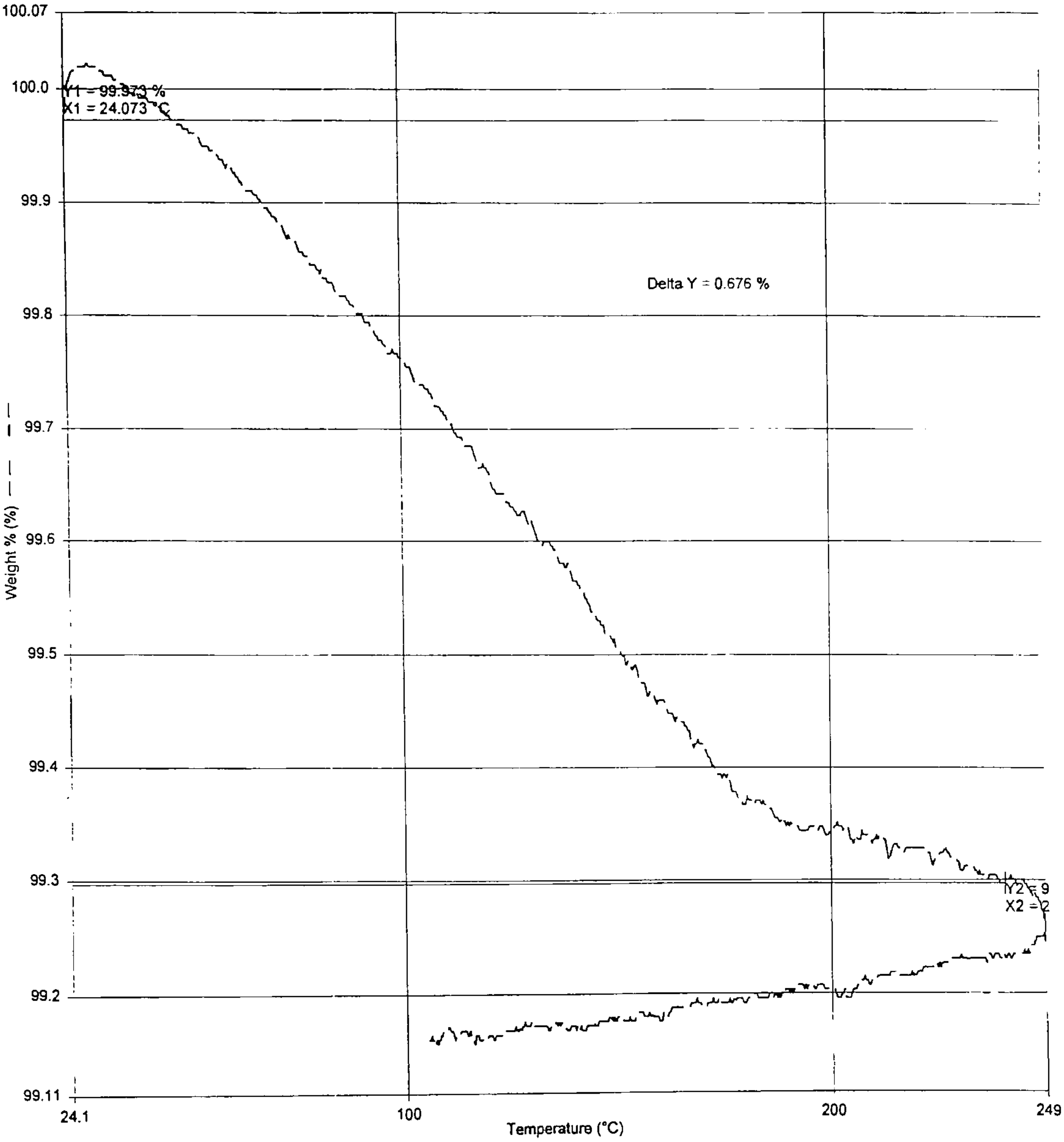
6/24/98 12:35:42 PM

Filename: C:\PE\Pyris\..\QSAVE@980619095045.TGD
Operator ID: rjw
Sample ID: test C 1 - MELINEX PET 48 ga
Sample Weight: 4.106 mg
Comment: ICI MELINEX PET
48GAUGE / MP 255-260 C



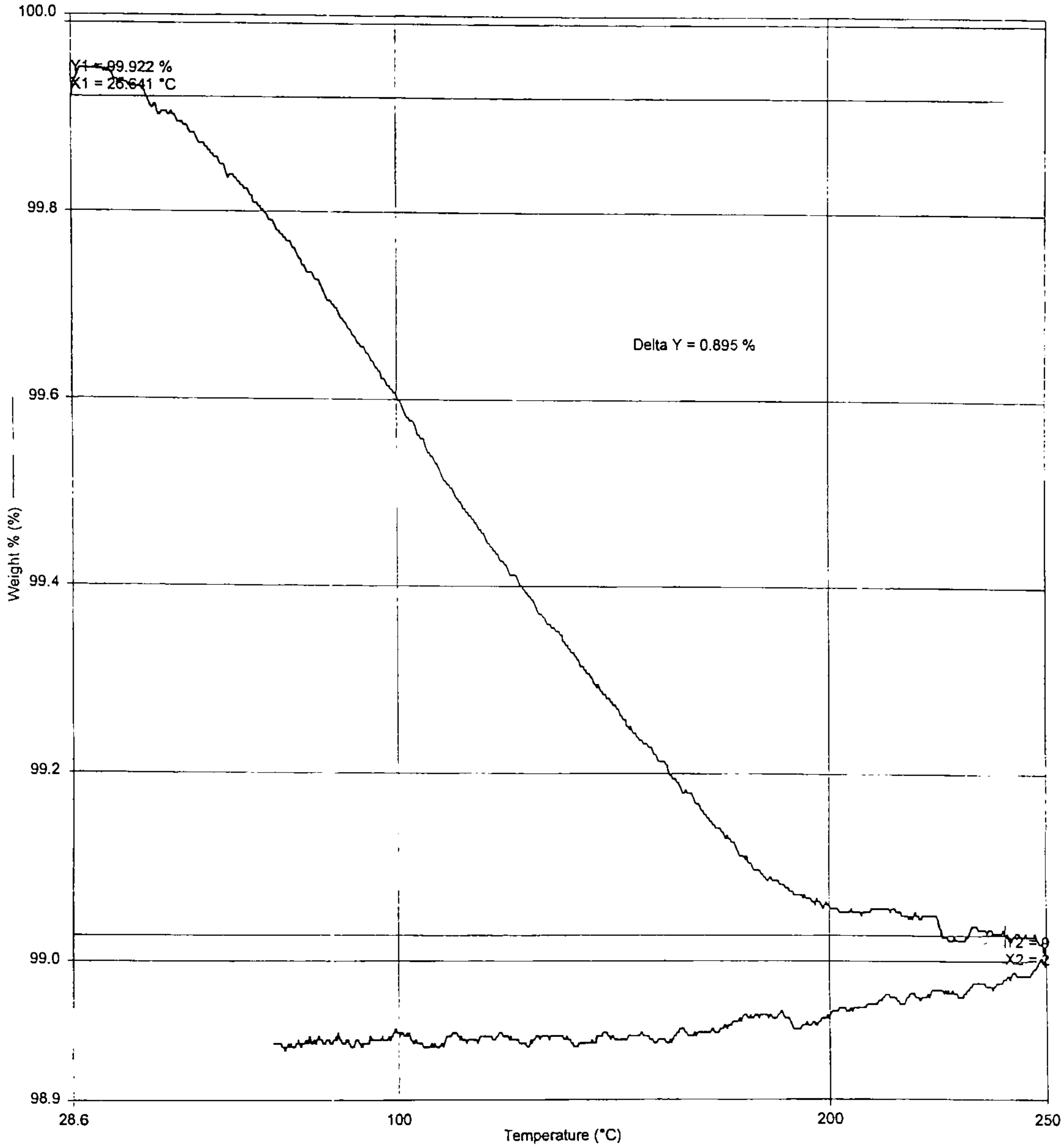
1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min
6/24/98 12:36:45 PM

Filename:	C:\PE\Pyris\..\QSAVE@980619104155.TGD
Operator ID:	rjw
Sample ID:	test C 2 - MELINEX PET 48 ga
Sample Weight:	4.130 mg
Comment:	ICI MELINEX PET 48GAUGE / MP 255-280 C



1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min
8/24/98 12:37:25 PM

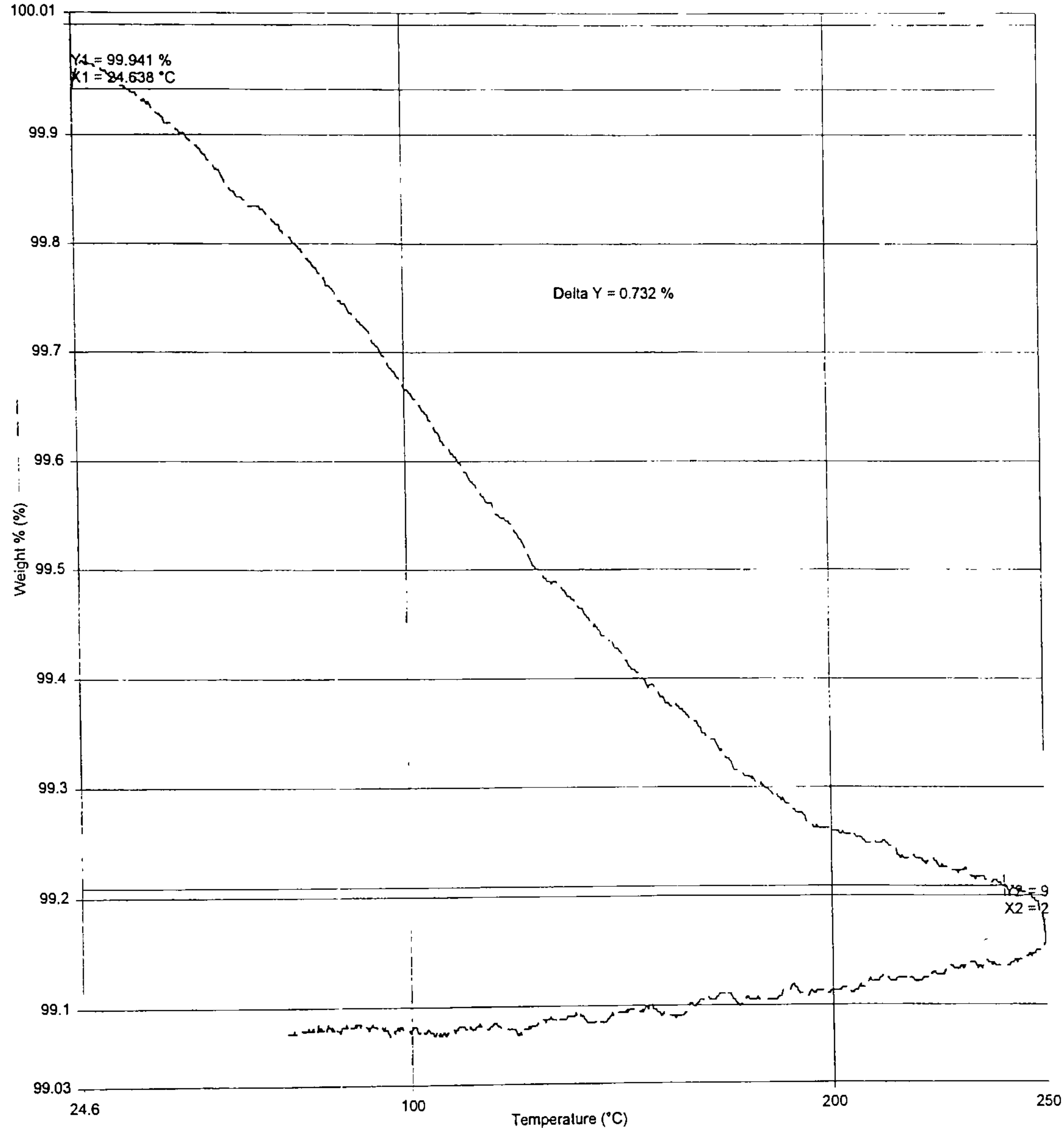
Filename:	C:\PE\Pyris\...\QSAVE@980619111841.TGD
Operator ID:	rjw
Sample ID:	test D 1 - MELINEX PET 78 ga
Sample Weight:	4.279 mg
Comment:	ICI MELINEX PET 76 GAUGE / MP 255-260 C



1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min

6/25/98 3:13:05 PM

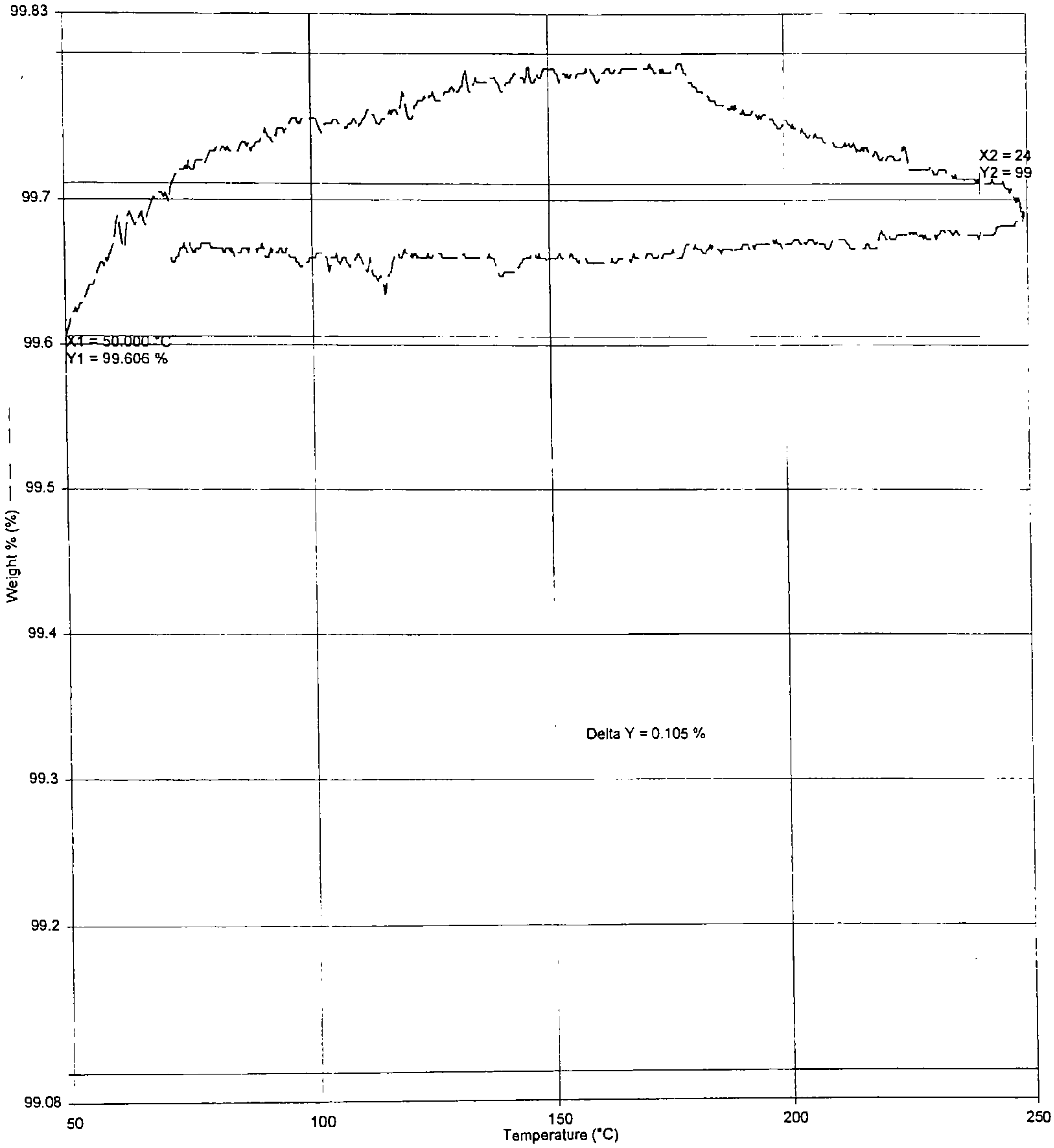
Filename:	C:\PE\Pyris\...\QSAVE@980619122523.TGD
Operator ID:	rjw
Sample ID:	test D 2- MELINEX PET 76 ga
Sample Weight:	5.721 mg
Comment:	ICI MELINEX PET 76 GAUGE / MP 255-260 C



1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min

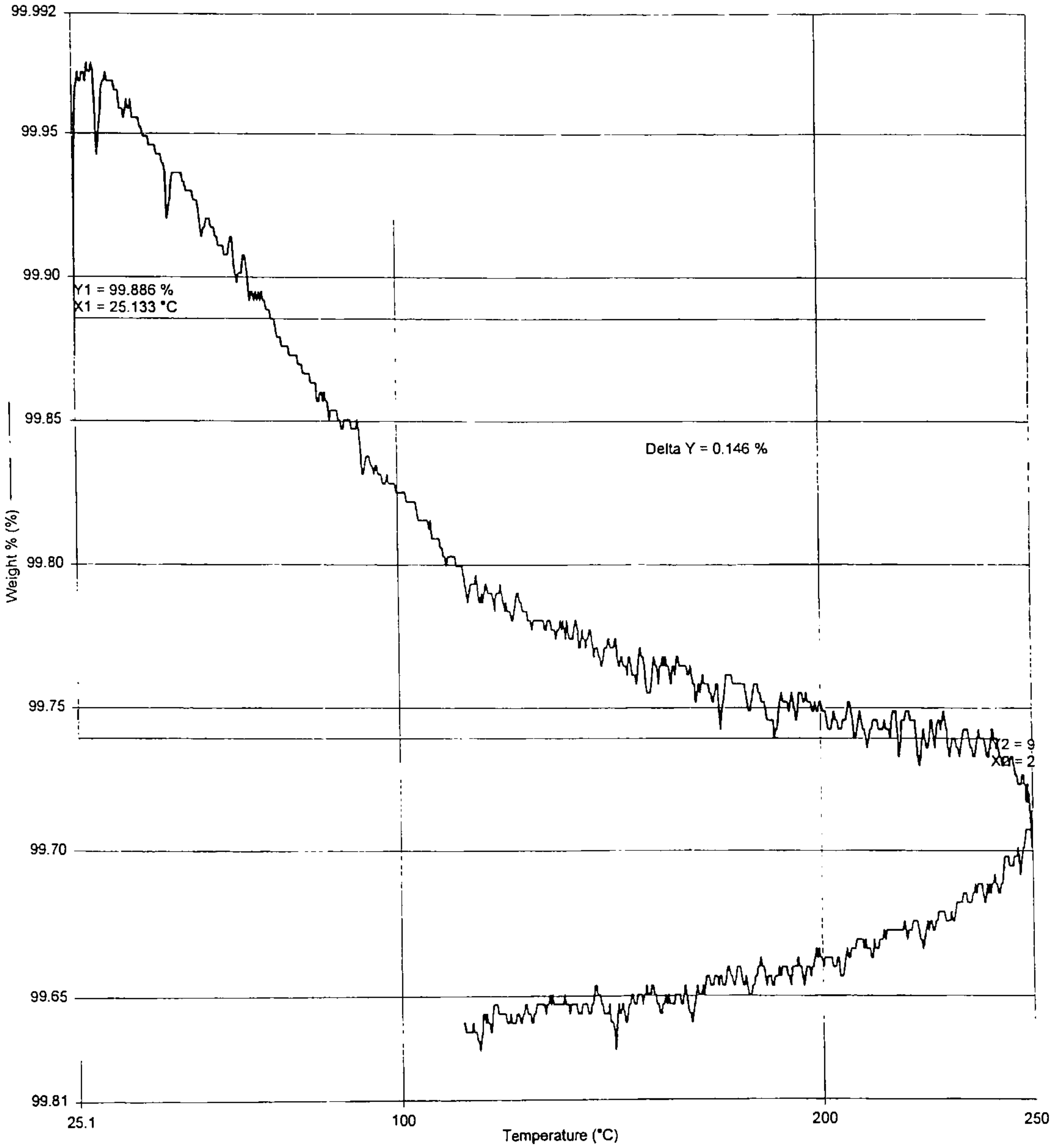
6/24/98 12:38:25 PM

Filename:	C:\PE\Pyris\...\QSAVE@980622150656.TGD
Operator ID:	rjw
Sample ID:	test E1 - LCP / VECTRA A-950
Sample Weight:	5.060 mg
Comment:	SUPEREX - LCP / VECTRA A-950(TICONA PELLETS)



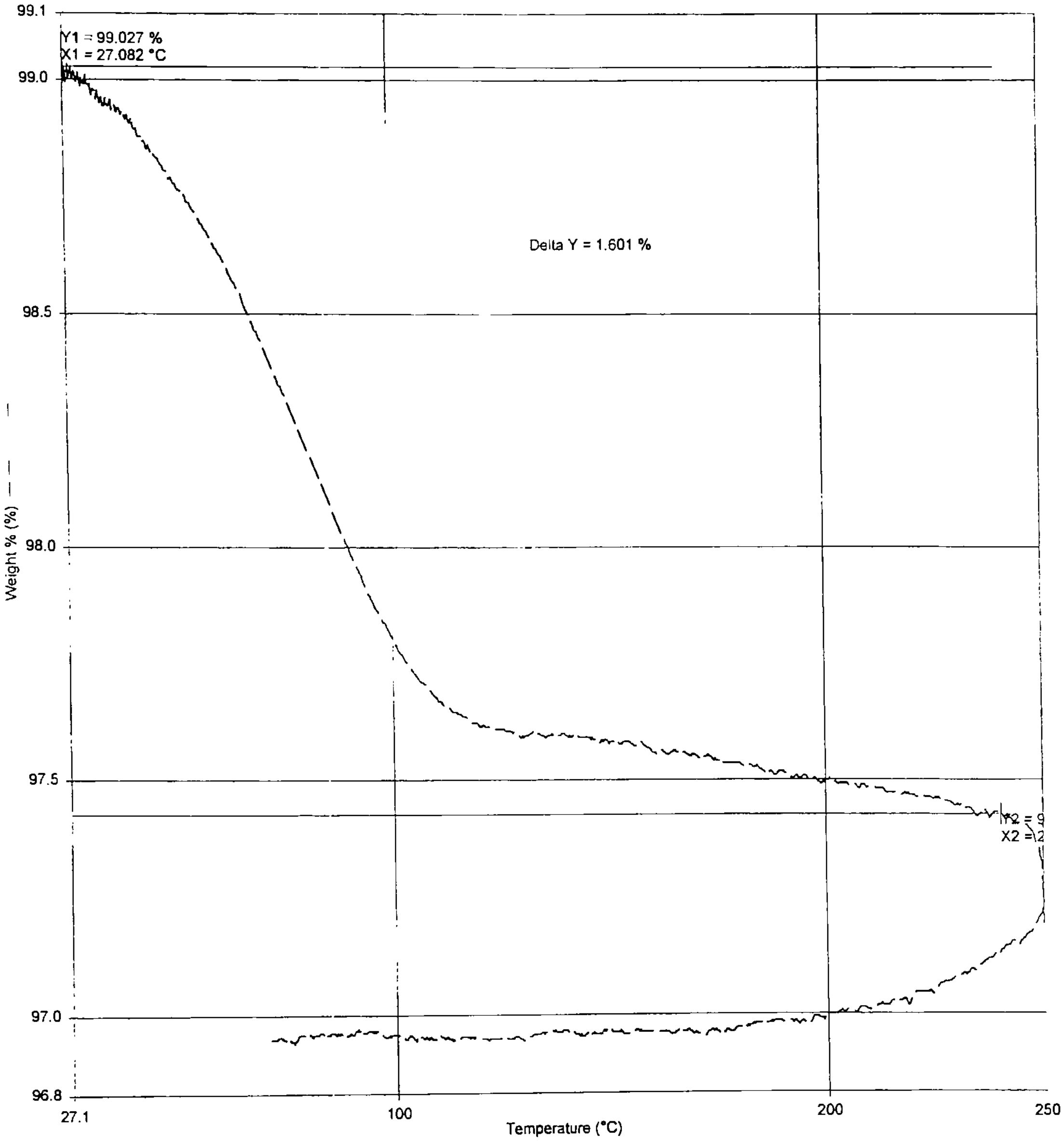
1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min
6/24/98 12:42:05 PM

Filename:	C:\PE\Pyris\...\QSAVE@980622155020.TGD
Operator ID:	rjw
Sample ID:	test E2 - LCP / VECTRA A-950
Sample Weight:	5.050 mg
Comment:	SUPEREX - LCP / VECTRA A-950(TICONA PELLETS)



1) Heat from 30.00°C to 250.00°C at 20.00°C/min 2) Hold for 1.0 min at 250.00°C	3) Cool from 250.00°C to 30.00°C at 20.00°C/min 6/24/98 12:42:52 PM

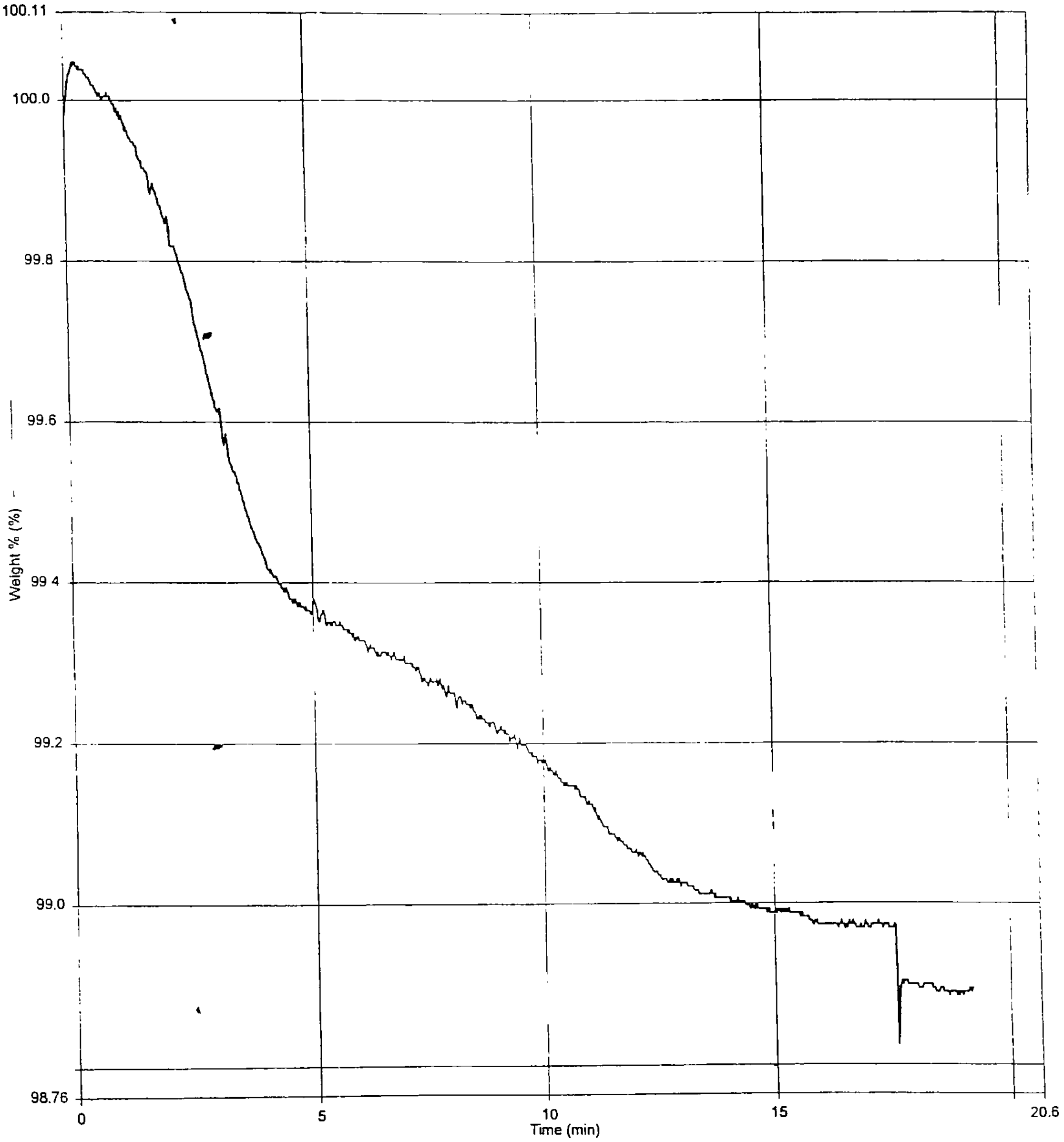
Filename:	C:\PE\Pyris\..\QSAVE@980622095920.TGD
Operator ID:	rjw
Sample ID:	test F1 - PP 150ASB-X
Sample Weight:	3.499 mg
Comment:	MOBIL BICOR - 150 ASB-X MP



1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min

6/24/98 12:39:15 PM

Filename:	C:\PE\Pyris\...\QSAVE@980622144003.TGD
Operator ID:	rjw
Sample ID:	test F2 - PP 150ASB-X
Sample Weight:	3.443 mg
Comment:	MOBIL BICOR - 150 ASB-X



1) Heat from 30.00°C to 250.00°C at 20.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 30.00°C at 20.00°C/min

6/22/98 2:59:13 PM

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