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## INTERACTIONS IN PACKAGING SYSTEMS –“LIVELY ENCOUNTERS”<sup>†</sup>

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### Abstract

The containment of less aggressive fluids (fruit juices, dairy produce) in cellulosic carton-board materials has been achieved for some time with considerable success. More recently, attempts have been made to contain the more fugitive liquids (paints, inks, oils, detergents and additives) in similar carton board structures. Factors related to the successful containment of ‘aggressive’ fluids have been investigated and various conclusions drawn. Also considered are the transport behavioural characteristics of fluids that success in penetrating the internal barrier of the carton assembly. This has allowed re-definitions of the concepts associated with damage and failure for a wide range of composite fluids.

### Introduction

A packaging product can be any item that encloses a product for transport, aesthetic purposes or preservation needs. Several general forms of classification can be used to describe the wide variety of packaging products available. These classifications split the products, usually into three groups, transport packages, multi-component packages and consumers packages. The study undertaken concerns consumer packages.

<sup>†</sup> Dedicated to the memory of Professor Dr. Anton Šebenik

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Essentially, packaging systems that are based on erected and printed carton-board substrates are of a semi-rigid construction. Carton boards are used throughout the industry to provide high quality, cheap, yet strong packaging systems. Carton boards can be made from a variety of different grades of pulp. Due to environmental pressures, more and more carton boards are being produced from recycled grades of cellulose pulp.

It must be recognised that many types and forms of polymers and macromolecular materials are used extensively in today's packaging industry. The requirement of extended shelf life, along with special packaging needs, means that the technology required has had to develop to meet these needs. This is clearly evident in the packaging of liquids. The producers of liquids require packages that are cheap, strong, aesthetically acceptable and environmentally sound.

Whilst the main thrust of this paper is the containment of relatively hostile liquids in modified carton-board packaging assemblies, attention needs to be given to other alternative packaging systems. Each of these packaging systems should be developed on the basis of interactions that take place within the container, and on the surfaces of the container system. These interactions will occur over different time scales and to different extents.

Consequences of such interactions will be partly dependent on external factors such as the temperature and on any pressure driven processes occurring within the total packaging system. Since the packaging system, by definition, consists of the contained and the container, interactions can take various forms. It is possible to monitor such interactions by following changes in the nature of the container, and of the contained, by various analytical methods and by various routes to characterisation. Packaging protects the contents against air, water, relative humidity, odours, micro-organisms, insects, light, compression and impact. Packaging also aids in containing desirable components of the product constituents such as the colour, the flavour, the form and the structure. Packaging is also usually required to inform and designed to inform. The user of the packaged system may need information regarding the contents. Such information could include warnings associated with hazards, nutritional levels, dosage requirements, processing instructions, shelf-life features,

storage requirements and so on. The outer surface of the carton or packaging system can also give a good indication of the nature of the contents of the container from the point of view of advertising and representation of the contents.

In this way, the more important aspects of packaged systems can be identified. These are the packaging container itself, the contents and the images created on the surface of the packaging system. Clearly, the packaging system is designed to contain. This implies that a significant barrier feature should be incorporated into the packaging system.

Use of this approach provides a reasonably firm basis for considering the significance of interactions within and between the various components of the package system. Thus we can consider interactions within the substrate, interactions within barrier coating systems and interactions within the printed surface, or coatings. We can also consider interactions that take place within the contents of the package. Of great importance are the interactions that occur between each of these separate zones. It is at this point that the nature of formulation and of formulation optimisation can be considered. Each part of the total packaging system is designed to fulfil various objectives. In reality the total packaging assembly is a compromise. For compromises to be effective, they need to be understood. Packaging systems are no exception to these guidelines. Similar points can be raised with respect to the contents of the package.

Packaging, in its sophistication, reflects the needs of human societies and their technical ability to provide for these needs. The nature of the product supply system, the methods of commodity preservation, and the availability of packaging materials determine the packaging systems that are used. While some of the features of modern packaging are concerned with the use of graphics and information technology, for consumer appeal and for additional design feature for operational convenience, the packaging industry must always be aware of the need to contain those products that society requires. Thus, at least for the foreseeable future, there will always be the need for ceramic materials, for plastic materials, for carton board materials, for metallic materials and so on.

Packaging materials can be classified according to whether they are flexible, or rigid. Rigid materials include the ceramics, such as glass, and metallic materials. The more flexible materials include, poly(ethylene), poly(propylene), copolymers of various types, regenerated cellulose films (either in plain state or in coated forms), nylon films, polyester films and polycarbonate films.

There are also those materials whose properties lie somewhere between these two extremes of flexibility and rigidity . Examples include metal foils, rigid polymer systems such as high-density poly(ethylene) and laminated assemblies, for instance those based on metal foils laminated to flexible packaging films. The use of co-extrusions in packaging has increased rapidly from the late 1970's. In co-extrusion, two or more thermoplastic materials are extruded simultaneously. Co-extrusion can provide an intimate combination of materials in precisely the quantities required to function. Incompatible plastic materials can be bonded using thermoplastic adhesives. Several layers of such films may be included in the final packaging format. Examples of application include films of ethylene-co-vinyl alcohol and white-pigmented, low-density poly(ethylene), used for the packaging of frozen vegetables and fruits. In these applications, one layer imparts toughness, opacity or stiffness and another, or other layers, provide heat stability. In another example, co-extrusions of nylon and poly(ethylene), in five layers are used for thermoforming where a high gas barrier and water vapour barrier are required, for instance in the packaging of medical products.

There is another type of interaction that needs to be considered within the realm of lively encounters. This is the interaction between the user of the packaging system and the packaging system itself. Certain questions can be asked:

1. How user friendly is the packaging system? For example how easy is it to acquire access to the contents of the container?
2. How legible is the information on the outside of the container?
3. How well does the design on the front of the container represent the contents?
4. What is the storage stability of the container system?
5. What are the handling properties of the container system?

Questions may also be asked about the security of the packaging system.

1. How tamper-proof is the system?
2. How secure is the information provided on the outer surface?
3. How well can one define the contents of the packaging system?
4. Is it possible to monitor the history of the packaging system and the contents from the point of its construction and filling to the point of its use?

The packaging system is composed of substrates, of coatings, of barrier fluids, of inks and of varnishes. In addition, there are the contents of the package system that may be solid, liquid or gaseous or mixtures of these components. The contents of the packaging system may be composites. They may be complex. They will be mobile over various time scales.

One area that encompasses many of these factors is the characterisation and optimisation of carton board composite packaging, particularly with respect to the containment of liquids. This point is the subject of the current study.

Aspects relating to the containment of commercial liquid systems, within cartons manufactured from polymer coated carton-boards, have been studied. Consumer pressure to use environmentally sensitive packaging assemblies has created a large and expanding market for renewable, recyclable or biodegradable materials. The need to reduce the amount of non-disposable materials is ever increasing.

Carton boards manufactured from cellulosic wood fibres fulfil many of the requirements of primary recycling. Cellulose is biodegradable. Packaging made from cellulosic fibres has therefore been extensively used to contain non-perishable goods. Unfortunately, due to the high gas permeability and hydrophilicity of carton-boards, perishable and liquid goods cannot be contained in simple cellulosic containers.

To overcome these difficulties, polymer barriers such as poly(ethylene), ethylene-co-vinyl alcohol polymers and poly(propylene) have been developed to be used with carton board systems. By co-extrusion of the plastic components onto carton board surfaces, packaging systems can be made that are able to contain perishable and liquid goods. The containment of liquid systems requires a high integrity of package design. Any defects or imperfections in the polymeric barrier coating could result in loss of liquid containment or in diminution of the qualities of the liquid contained. Once the liquid has entered the cellulosic carton board structure, failure becomes inevitable.

The complexity in erecting and sealing polymer-coated, carton-boards designed for liquid containment, leads to difficulties in obtaining full integrity. Therefore, the nature and characteristics of liquids that are contained or transported within polymer carton board cartons need to be investigated so that the models of containment failure can be established and understood.

The chemical properties of cellulose and cellulose derivatives are not fixed, due to influencing factors such as degradation from age, heat, light, air acidity etc. The cellulose matrix is an interacting matrix. It is a changing matrix. When left in acidic media cellulose degrades to a product of lower molecular weight. Cellulose is susceptible to attack by oxidising agents. Such attack causes breakdown of the cellulosic chain. When cellulose undergoes heat treatment the tensile strength and swelling ability are greatly reduced. This is because of increased hydrogen bonding between cellulose molecules, and because of the formation of chemical bonds between adjacent molecules.

Adsorption and absorption of liquids by the cellulosic component of the carton-board system, with subsequent swelling of the cellulosic component, are important phenomena in the carton-board manufacturing process and in carton-board use. Adsorption and absorption have repercussions with respect to the barrier properties of final carton board products and also to the ultimate strength of the carton board system. Swelling can occur in the more ordered regions or in the less ordered regions of the cellulosic system. The less ordered regions will swell the most due to greater preferential adsorption in this area. Polar gasses and liquids are adsorbed to a greater extent compared to the non-polar gasses.

Cellulose is one of the more hydroscopic substances and will absorb moisture, even from drying agents such as phosphorus pentoxide. The absorbed water is held in the fibre as bound water, capillary encased water, or imbibed water. This point is important for cellulose carton board systems. Bound water is water that is absorbed directly onto the surface of the cellulose ordered zones and is usually approximately 3-4% (w/w) of fibre. The interaction is very strong, with the water having different properties from that of free water. The bound water has a higher density, does not respond to humidity changes and is only removable at very low vapour pressures. Bound water causes swelling and effects the physical properties of the fibre.

Capillary water is the water that is in excess to the bound water. It is not adsorbed, but lies in the narrow capillaries of the fibre. It causes less swelling and keeps the properties of free water.

Even after the fibres have absorbed all the water they can sustain, from saturated water vapour, they can still absorb 200-300% of the fibre weight if water, in its liquid state, is placed into contact with the fibres. This is known as imbibed water. This water fills the fibre pores and remains as 'free' water. Once the fibre pores are filled, then water is taken up by imbibition with no more swelling. The point at which this occurs is known as the fibre saturation point. It has been shown that absorption of water, by cellulosic systems, is an exothermic process and so is inhibited at high temperatures.

From the point of containment in cellulosic carton boards, it is important to recognise that cellulose also swells in salts, acids, alkalis and organic bases. Highly hydrated ions cause the most swelling. Anions have a greater effect on swelling relative to the swelling provided by cations. Some cations, such as calcium cations inhibit swelling. Strong mineral acids, can dissolve the cellulose with degradation occurring. Bases that cause swelling include sodium hydroxide and those quaternary amines that possess large groups, attached to the water solubilising entity, such as dimethyl dibenzyl ammonium hydroxide.

Many fluids required to be contained by cellulosic systems can be classed as hostile in that they contain acidic components, or because they contain basic components. It is common for them to have surfactant systems included in their total formulation. Such materials have a dramatic tendency to modify the properties of the cellulosic component, should they come into contact with the cellulose component. Packaging systems must be designed to prevent such contact.

Appearance properties affect the overall look of the carton board. It is important that the final packaging product looks good. In virtually all cases, carton board is used to produce a commercial package representing an image. The package will protect and form a transport device for the medium within.

## Board Properties

Packaging products made from cellulosic materials are increasingly being modified and improved. Improvements are based on appearance and chemical and physical criteria. Parameters such as whiteness, gloss, smoothness, chemical nature, strength, elasticity, and printability are all properties that are manipulated to achieve optimum performance for a particular packaging product. The properties of a carton board are directly related to the basic raw material used in its manufacture. The appearance and mechanical properties of multi-ply carton-board systems are often dependent on the quality and type of pulps used. The source of cellulose used for carton-board manufacture can greatly influence its properties. The properties of carton-board can be grouped into two categories, appearance properties and performance properties. Appearance properties can be split into printability and varnishability, whiteness, surface structure and smoothness, adsorption, drying behaviour, and rub resistance. Performance properties can be subdivided into strength and toughness, stiffness, box compression strength, creasability and foldability, flatness and dimensional stability, runability, sealability, and barrier characteristics.

Appearance properties affect the overall look of the carton. It is important that the final packaging product looks good. In virtually all cases, carton-board is used to produce a commercial package representing an image. The package will protect and form a transport device for the medium within.

This study is concerned with the containment, in carton board packaging systems, of commercial and domestic detergent systems. For this reason, several types of carton board were investigated, as were several detergent systems.

Production and development of board systems were examined in detail. Each board was of a multi-ply type, both sides of the carton board system being covered by polymeric coating. The polymeric coatings were applied through extrusion coating for all the carton board types. The carton boards were supplied in their coated form.

All the boards used in this study had a grammage of  $300\text{g/m}^2$  and a thickness of 500 micrometers. The underlying cellulosic components were coated with a thin layer of poly(ethylene) on the upper surface, while the lower surface was coated with a



polymeric composite. The upper surface of the board becomes the outer surface of the carton when assembled. The polymeric coating on this outer surface is designed to receive and to accommodate printed material, and also to act as a secondary barrier to liquid escapement. The lower surface of the board becomes the inner surface of the carton when assembled. This surface is designed as the primary barrier to liquid escapement.

The composite barrier coatings used on the lower surface of the boards were all multi-component systems that were produced by melt coextrusion processes. All the coatings were composites of two or more polymers, with one polymer being the active barrier to fluid systems. Table 1 lists the composite barrier coating compositions used.

<i>Table 1 Barrier Composition</i>	
<b>Inner layer</b>	Layer attached to cellulosic board
<b>Middle layer (if present)</b>	'active' barrier polymer
<b>Outer layer</b>	Layer in direct contact with contained liquid. Also, the polymer primarily responsible for heat sealing during carton assembly

For liquid packaging cartons, the main barrier to escapement of the fluid is the containment system that is used on the inside of the package. Once through this barrier, the fluid will diffuse. If the container is built around a cellulose base that is coated, the liquid can quickly diffuse through the cellulosic core, if the coating is compromised or perforated. The barrier coating can therefore be seen as providing the rate-determining step in carton failure. For this reason, particular attention needs to be paid to the examination of barrier coatings, along with the board systems to which they are applied.

### **Contained Fluids**

Not all liquids can be contained within carton board assemblies. Some liquids are containable, others are not. To attain an understanding of the nature of interactions within carton board substrates designed to contain fluids, and therefore an

understanding of carton failure, it has been necessary to evaluate a wide range of liquid products with respect to containment in polymer coated carton board cartons. These investigations have centred around discovering how carton failure relates to the physical-chemical characteristics of the liquids to be contained, and to the kinetic processes involved in transport.

Each of these situations is one of interaction. For this study, the test liquids were placed into three categories according to whether it was felt that they could be contained in a liquid packaging system or not. Liquids that could be contained were termed 'non aggressive'. Liquids that were felt could not always be contained were termed 'aggressive'. Liquids that could not be contained at any time were termed 'very aggressive'.

The method of assessing carton failure involved placing the liquid carton assembly into an oven set at 40°C, for one month. If, after this time, the contained liquid managed to wick or diffuse into the cellulosic board matrix, then a failure was recorded. This process was repeated using four similar carton/liquid assemblies. If all the assemblies passed, then the liquid was termed 'non aggressive', if all five failed then the liquid was denoted as being 'very aggressive', if at least one failed, but not all, then the liquid was termed 'aggressive'.

### **Carton Assembly**

The carton assemblies under investigation were constructed of polymer coated carton board. Seals on the carton are produced by heat sealing of the polymeric coating. Due to the nature of the sealing process, a continuous polymeric film is not always produced in the seal areas. Any defects in the polymeric film could cause carton failure.

With multi-layer processes, care must be taken to match the melt viscosities of the various polymers used, to give a good uniform multi-layer structure. These multi-layer structures can be created by coating processes, by lamination and by coextrusion. Polymers that can be used together with the ethylene-vinyl alcohol copolymer include poly(propylene), low density poly(ethylene), high density poly(ethylene), polyamides and poly(ethylene terephthalate). These polymers help to

add strength to the barrier film while the ethylene-vinyl alcohol copolymer gives the barrier properties.

Before the polymeric coated carton-boards are manipulated into a carton form, they usually have a commercial design printed on to them. The design covers the outer part of the carton, so print is carried on the upper surface of the carton board. The upper surface of the carton board has a thin layer of poly(ethylene), which requires corona treatment to make it wettable by the inks. The surface is then printed using the offset lithographic printing method. The inks used may be convention in type, with respect to their method of drying or they may be curable through exposure to UV-irradiation. These processes produce high quality prints. The carton boards are supplied in sheet form. On-line varnishing or off-line varnishing can be used to add gloss and to protect the printed surface. UV curable varnish systems are often preferred for this stage.

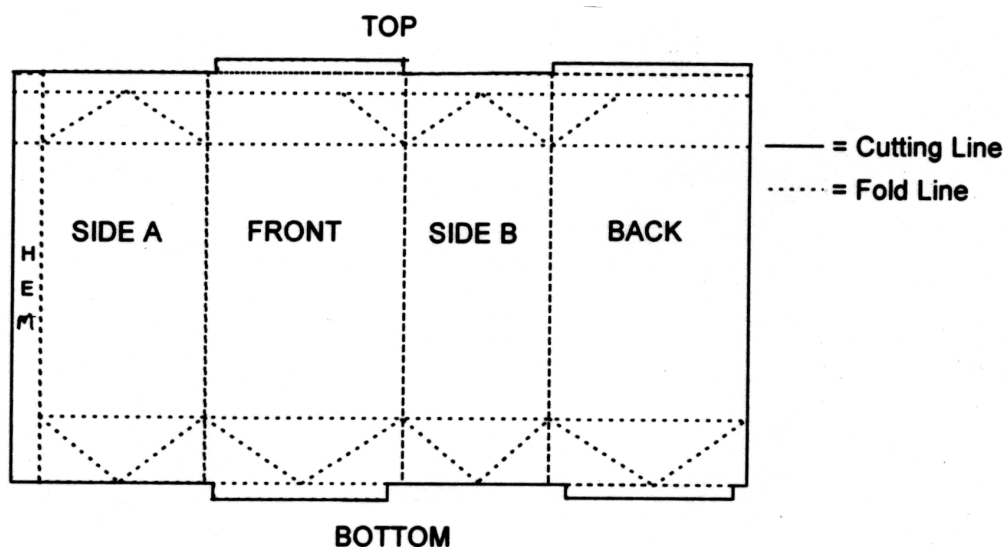
Within such printing, curing and coating systems, there are many types of interaction operating. We have interactions within the inks, within the coatings, interactions brought about by the corona discharge treatment and interactions brought about by the printing method. Each of these interactions will have a time dependency associated to the development of necessary interactive events. There will be rheological, film foaming, wetting, adhesion, drying and curing characteristics associated with these interactions. Indeed, the original coating of the carton board by the coextrudate poly(ethylene)-vinyl alcohol copolymer, or by the poly(ethylene) layer is another example of interaction within the fluid system and between two different components. Eventually the total carton system is a solid state composite system. This solid state situation has been achieved by taking other solid state components and transferring them into liquid or melt stage before the recreation of a new solid state composite. Each one of these operations has interactive implications.

Once printed, the carton board sheets are cut and creased in preparation for carton erection. Features of interaction arise in that the creasing and cutting must be carried out in an extremely precise way, otherwise failure in the finally assembled article is bound to occur. Factors such as stiffness, the grain direction, the moisture content, the thickness, the cellulose source and the polymeric coating type all affect the cut and

crease process. Therefore, the cut and crease process needs to be optimised for each carton board type.

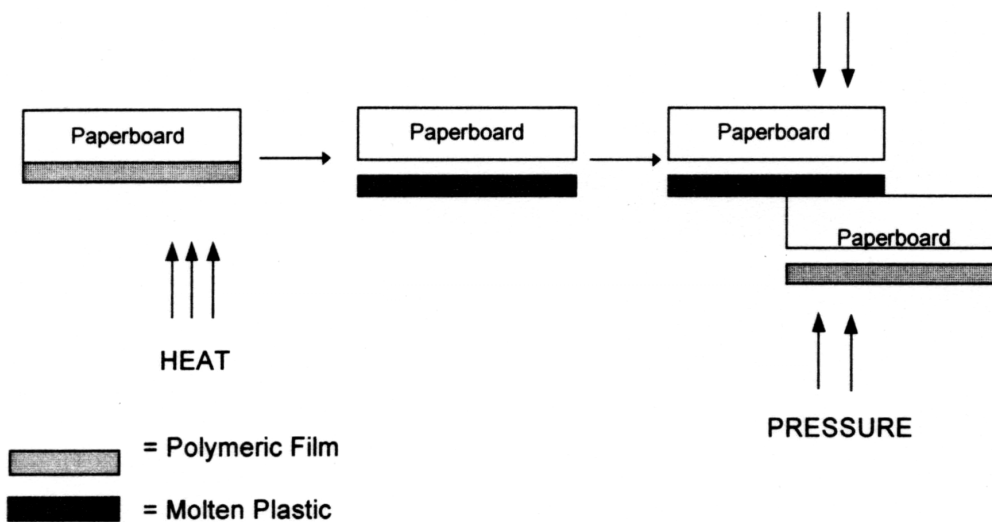
Figure 1 gives an indication of a standard carton design. The cut and crease processes provide a flat carton shape with strategically placed folds. The next state of the packaging process is to erect the basic carton shape by folding the flat carton base into a rectangular shape. Here, the two parts of the board are brought together to form a seal. A physical weld, or interaction is produced by melting the polymers along two of the edges and bringing the edges together. This process is carried out on a specially designed unit that has several functions. The different sections of the unit are:

- 1) the feed section in which the carton structures are fed into the conveyor unit,
- 2) the pre-fold section in which the vertical creases, as shown in Figure 1, are folded so that the edge of side 'A' and the edge of the back section come together
- 3) the hemming section, in which a bell knife skives half of the thickness of the board, just past the hem crease. This aids adhesion or interaction when the hem is brought into contact with the melt polymer on the back section of the board.



*Figure 1 Die-cutting and creasing pattern for liquid packaging cartons*

A finishing operation now follows. The hem and the edge of the back section are pressed together to form a seal that is nipped. In this, nip rollers press and cool the newly formed seal. Here, the polymeric coating solidifies to form a watertight seal along the length of the carton. This section is followed by delivery, at which the carton is removed from the end of the unit and the basic rectangular carton structure has now been made. This process is continuous. There is a high through-put rate compared to that provided by other sealing methods. A representation is shown in Figure 2.

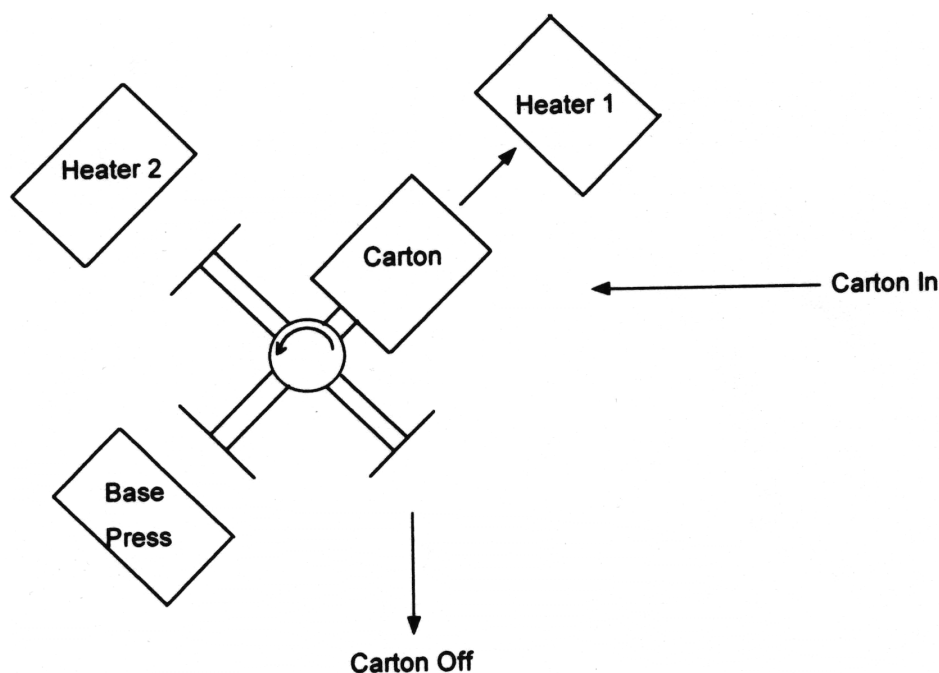


*Figure 2 The sealing operation using polymeric coatings*

The sealing of the carton top and of the carton base is a more complex procedure and requires specially designed facilities. In a typical operation, the rectangular erected cartons enter the unit and undergo a series of heat-sealing events. The basic structure of the unit is represented in Figure 3. The semi-constructed carton is placed on a rotating platform, shown in Figure 3, with the carton base facing outwards.

The heaters are hot air heaters and sealers and produce electrically heated air. The temperature of the heaters varies according to the board type, but is generally between 200-300°C. The folding section produces two triangular flaps within the carton. It is possible for a pinhole to appear at the point of these flaps. Should such events occur, these can be found by standard test procedures involving the use of specific dye solutions in staining tests.

The carton now has a sealed base and is ready for filling with the liquid product. This process is carried out in line. The carton is moved from the rotating platform, placed on a conveyor belt, and the liquid to be contained pumped into the carton. The top of the carton is then heat-sealed using hot bar sealers. These are electrically heated jaws that clamp the top of the carton and produce a heat-sealed union.



*Figure 3 Sealing unit – basic representation of heating/sealing section*

### **Characterisation Methods**

Various methods were used in the characterisation of the carton boards, the assembled carton board systems and the contained fluids.

### **Surface tension and contact angle studies**

The surface tension of each of the detergent fluids was assessed using a du Nouy tensiometer. For each measurement, 20 cm<sup>3</sup> of test liquid was used. The temperature of the test liquid was adjusted to 20°C before each measurement, and measurements were taken at 20°C. All the liquids to be contained were examined using this technique.

For each liquid, ten readings were taken and a mean surface tension value recorded. The results were then evaluated with respect to carton failure. Reference liquids were also examined and the results compared to literature values for their surface tension. Static contact angle measurements were also carried out on the test fluids, and for the detergent systems, using the surface of the carton boards. A Contact- $\Theta$ -meter was used for this work. This device works by a beam of light impinging on the droplet that is placed on the solid surface. The light beam is then reflected at an angle that can be related to the contact angle. The reflected light beam is detected visually, using an eye-piece that revolves over the droplet. The eye-piece is attached to an electronic sensor that measures the angle of detection. The apparatus was calibrated so that an LCD system displays the contact angle.

For each test solution, a 3 cm  $\times$  5 cm piece of polymer coated carton board was used. Ten drops of each test solution were placed on the polymeric barrier coating. After deposition of each drop, the contact angle was measured using the Contact- $\Theta$ -meter. The droplets were applied to the coating by way of an analytical syringe. This allowed the volume of the droplet to be constant for each reading. The contact angle for each droplet was recorded and the average calculated. The value obtained was recorded as the mean contact angle.

The final results were correlated to the surface tensions of the liquids. Following this, the critical surface tension of the polymeric coating and the solid wet tension of the polymeric coating were determined. The Zisman method was used to determine the critical surface tension of the boards, and the Kaelble method was used to determine the surface tension of the boards themselves. By using the Kaelble procedure, the work of adhesion at the interface between the fluids and the substrates could be determined. Table 2 gives information of the surface tensions of various reference test liquids used in board evaluations, specifically with the respect of the determination of  $\gamma_c$ , the critical surface tension of the boards.

**Table 2 Surface Tension of Reference Test Liquids for Critical Surface Tension Analysis**

Solvent	Chemical Formula	Surface Tension (mNm <sup>-1</sup> )	Polar/Disperse Ratio, $\beta_L^1/\alpha_L$	$\alpha_L^2$
Ethoxy propyl acetate (EPA)	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	28.5		
EPA:TP at 1:1	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub> : (CH <sub>3</sub> C <sub>4</sub> H <sub>6</sub> ) <sub>3</sub> PO <sub>4</sub>	34.1		
Tritolyl Phosphate (TP)	(CH <sub>3</sub> C <sub>4</sub> H <sub>6</sub> ) <sub>3</sub> PO <sub>4</sub>	43.7	0.04	12.52
Poly(ethylene glycol) (PEG)	HO(CH <sub>2</sub> ) <sub>n</sub> OH	48.0	0.64	11.91
PEG:Formamide (FA) at 1:1	HO(CH <sub>2</sub> ) <sub>n</sub> OH : HCONH <sub>2</sub>	51.2		
Formamide (FA)	HCONH <sub>2</sub>	59.1	0.48	-
Glycerol	HOCH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	63.4	0.71	11.66

1.  $\beta_L$  is the square root of the polar component of the surface tension of the liquid
2.  $\alpha_L$  is the square root of the dispersive component of the surface tension of the liquid

## Thermal Analysis Studies

Differential scanning calorimetry was used to examine the thermal properties of all the composite barrier coatings over a wide range of temperatures. The instrument used was a Du-Pont 2000 unit located in the Colour Chemistry Department of the University of Leeds. The temperature programme used involved heating from room temperature to 300°C at a rate of 10°C per minute. A nitrogen purge of 0.2 dm<sup>3</sup> per minute was used.

Each of the polymeric, barrier-coated, carton-board systems was assessed by differential scanning calorimetry.

## Particle Size Analysis Studies

Particle size analysis was carried out on all of the liquids tested. For each programme run, 1g of test liquid was dispersed in 150g of electrolyte. The electrolyte used was an Isoton 2, azide free, balanced solution. A Coulter multisizer was used to provide



particle sized distribution curves for the particular samples tested. The experimental procedure used for each programmed run was as follows:

The test liquid was added to the glass analysis vessel. This test solution was mechanically stirred for 3 minutes to ensure good dispersion of the test liquid. Following this, the conductant sensor was activated for 100 seconds and the data accumulated.

For each test liquid, useful data were recorded. The results obtained were evaluated with respect to interactions within the liquid packaging assembly. Links between particle size distribution and carton failure were also investigated.

### **Viscometric Studies of Solutions and of Dispersions**

The viscosity of a liquid has been described as its resistance to flow when subjected to a shear stress. The viscosity characteristics of fluids have implications for their containment ability in carton board packaging systems. Should the container fail, it is possible that the fluid can then undergo flow within the cellulosic components of the inner materials of the assembled carton board. This capillary controlled flow is dependent upon the viscosity of the fluid undergoing flow, as well as on the conditions under which such flow is taking place. The cellulosic matrix, that is part of the inner section of an assembled carton, is a mix of fibres and space with ample room for flow events to take place. The lower viscosity fluids will have a greater tendency to flow within these capillary sections than would the higher viscosity fluids. Other factors such as the temperature, the relative hydrophilicity/ hydrophobicity of the fluids and their tendencies to get involved in interaction with the cellulosic component are of significance.

For this work, four Ostwald viscometers were used. The four viscometers had different capillary sizes. These four capillary sizes were used to ensure that the recorded flow times exceeded 100 seconds. Each viscometer was calibrated. Viscosity measurements were undertaken for all the liquids tested. Measurements were taken at  $20^{\circ}\text{C}\pm 0.02^{\circ}\text{C}$ . For each liquid, five separate measurements were taken and a mean value calculated. The values were within 0.15 seconds of each other.

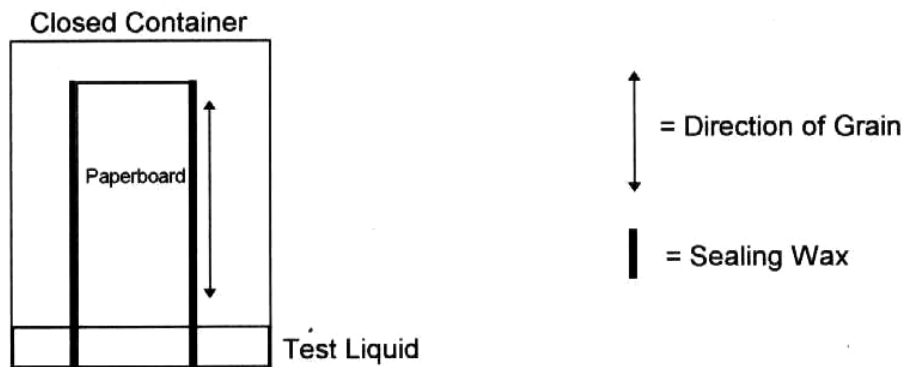
## Diffusion/Wicking Studies

The main form of failure of a liquid packaging carton is by wicking of the contained liquid through defects in the polymer barrier coating. The rate-determining step of that failure is that of liquid getting through the barrier coating. Once through the barrier coating, the liquid wicks across and through the cellulosic board. This process occurs as a result of the carton barrier coating failure.

It was thought that the liquid products generally pass into the cellulosic material via pinholes in the barrier coating. However, even when these pinholes are present, not all liquids pass through them. It is therefore evident that some liquids have a greater wicking ability than others do. Thus, they have a greater affinity for the cellulosic material. The cellulosic system provides a driving force for the uptake of liquid through the pinhole in the coating. By examining the rate at which test liquids wicked through the cellulosic board, it was hoped that differences between liquids that fail, and liquids that do not fail, would be shown.

For the diffusion study simple instrumentation was required. The approach involved the use of an accurate balance, screw top glass jars of 100 cm<sup>3</sup> and 250 cm<sup>3</sup> capacity, a conditioning oven, a temperature-controlled water bath and paraffin wax. A method was designed to measure how much each liquid would diffuse through a known amount of carton board over a specific time period. Each test strip was conditioned for 48 hours under standard conditions before weighing. For each test, a 3cm × 8cm sample of carton board was used. For all samples, the diffusion study was conducted in the direction of the grain of the carton-board in a manner shown in Figure 4. Studies against the grain showed minimal diffusion.

The test liquids entering the carton board samples needed to have such entry controlled. The carton board, once cut, had four edges that would be able to absorb liquid. To control the diffusion process, two of the carton-board edges were sealed using paraffin wax. The wax was melted, applied to the open cellulosic board and allowed to cool. This produced a moisture seal around the cellulose. The carton board samples had only one edge that was open to the liquid diffusion process. The specific layout is given in Figure 4.



*Figure 4 Cartonboard sample prepared for wicking study*

Each liquid to be studied was placed in a glass screw cap jar to a 1cm depth. The glass jar was then sealed and placed in a water bath, set at the desired test temperature. After a 24 hour time period, each board strip was removed from the liquid. Excess liquid, (not inside the board structure), was removed and the test strip placed into the control oven for 1 hour. The test strip was then removed from the control oven and weighed. The mass was recorded according to the time spent in the liquid. The test strip was then replaced into the test liquid and left for a further 24 hours. This process was repeated until 240 hours had elapsed, or until the liquid had wicked through the whole sample. Some liquid samples were measured over a period of one hour as their wicking rates were so high.

The standard wicking study was carried out at a temperature of  $20^{\circ}\text{C}\pm 0.2^{\circ}\text{C}$  for all the carton board/liquid combinations. A temperature dependence study was performed, using temperatures of  $30^{\circ}\text{C}$ ,  $40^{\circ}\text{C}$ ,  $50^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ , on a selection of the test liquids using the identified carton-board.

For each carton board/liquid combination, five separate test samples were used. The experimental data were acquired and the mean weight gain calculated at each time interval. In addition to these studies, an evaluation of the solids content, the pH and the density of each of the detergent fluids was undertaken.

## **RESULTS AND DISCUSSION**

### **Critical Surface Tensions of Board Assemblies**

The critical surface tension is an important parameter for characterising the wettability of a solid surface. By knowing the critical surface tension of a solid surface allows one to predict, to a certain extent, how a liquid will physically interact with that surface.

When a liquid comes into contact with a solid surface it can do one of two things. It can either spread or recoil. If it spreads, then the solid-liquid and the liquid-air interfacial areas increase and the solid to air interfacial area decreases. If the liquid is repelled then the reverse is true.

Detergent fluids are designed to wet. Whilst this is a good quality from the point of view of their intended application, it can be a problem when one is considering situations associated with the barrier properties of containment systems. For the co-extruded interlining barrier coatings used in the cartons involved in this study, there are several polymer interfaces that could have different critical surface tensions.

Table 3 gives the critical surface tension values calculated by the Zisman procedure for a series of carton board systems, in their native form and in their processed equivalents. From Table 3, it is clear that flame treatments activate the surface of the boards in question. This can be seen by comparing the value of the Enzo SBS flame seal area system with that of the native Enzo SBS board. Thus, the liquids will spread over the flame sealed areas more readily than they would over the non-flame sealed areas. If those flame sealed areas are regions of defect, then the effect of the defect is exaggerated by the improved wetting that would take place at those points.

Consideration of the Kaelble approach to wetting takes into account, to some extent, the additive contribution of the polar forces and of the dispersive forces to the critical surface tension and overcomes some of the shortfalls associated with the Zisman technique. Using the Kaelble approach, the solid wetting tension,  $\gamma_s$ , can be determined. Corresponding values for several standard solvent systems applied to various polymer barrier coating assemblies are provided in Table 4 for liquids on the

standard polymeric barrier coating and in Table 5 for liquids on the polymer barrier coatings that have been flame treated.

<i>Table 3 Critical Surface Tension Calculated via Zisman Plots</i>	
<b>Board</b>	<b>Critical Surface Tension at 20°C <math>\gamma_c</math> (mNm<sup>-1</sup>)</b>
Enso SBS	27.5
Enso Pankakoski	26.9
Enso oil barrier	29.4
Davidson/polycoat WLC	29.3
Davidson/polycoat oil barrier	29.1
Enso SBS – flame seal area	31.0
Enso Pankakoski – flame seal area	30.2
Enso oil barrier – flame seal area	29.7
Davidson/polycoat WLC – flame seal area	28.4
Davidson/polycoat oil barrier – flame seal area	29.1

The surface tension results for the untreated polymer coatings (Table 4) are similar to the critical surface tension results obtained using the Zisman procedure. There are slight differences, but the magnitude of these can be accounted for within experimental error. The polar disperse ratios of the solid wetting tensions are low for all of the polymers. This suggests that the solid surface is almost exclusively dispersive in character. Scrutiny of the solid surface tension results for the heat-sealed areas, (Table 5) shows that the values are higher than for the corresponding untreated polymer coatings. For the polymer coatings used on the Enzo SBS and Pankakoski boards, the value of  $\gamma_s$  is significantly higher than it is for the corresponding untreated polymer. This increase in activation is greater than that obtained using the Zisman approach. This could be due to recognition of the polar contribution of the solid surface tension. It was also noticed that the effect of flame treatment on surface characteristics of the board, in terms of surface tension, is dependent on the nature of the board. This can be seen from Figure 5.

*Table 4 Surface Tension for Liquids on Polymeric Barrier Coatings*

<b>Polymeric barrier coating</b>	<b>Liquid</b>	<b>Contact angle (<math>\theta</math>)</b>	<b>Work of spreading</b>	<b>Cos <math>\theta</math></b>	<b><math>\gamma_s</math></b>	<b>Polar/ Disperse</b>
Enso SBS	Glycerol	80.4	52.9	0.17	28.53	0.06
	Formamide	70.5	38.8	0.33		
	PEG	62.2	23.8	0.47		
	Tritolyl phosphate	48.1	13.6	0.67		
Enso Pankakoski	Glycerol	82.5	55.1	0.13	26.51	0.05
	Formamide	75.4	43.6	0.25		
	PEG	67.2	27.4	0.39		
	Tritolyl phosphate	52.4	15.9	0.61		
Enso oil barrier	Glycerol	75.4	47.5	0.25	31.7	0.06
	Formamide	69.5	37.8	0.35		
	PEG	54.8	18.9	0.58		
	Tritolyl phosphate	40.7	9.9	0.76		
Davidson/ Polycoat Wlc	Glycerol	79.4	51.7	0.18	28.72	0.03
	Formamide	75.4	43.5	0.25		
	PEG	66.1	26.6	0.41		
	Tritolyl phosphate	47.5	13.3	0.68		
Davidson/ Polycoat oil Barrier	Glycerol	78.3	50.5	0.20	31.15	0.03
	Formamide	74.8	43.0	0.26		
	PEG	60.3	22.6	0.50		
	Tritolyl phosphate	41.9	10.4	0.74		

Clearly, such variation in the effect of flame treatment is associated with the physical chemical nature of the coating used on the carton-board.

From the untreated polymer to the heat-treated polymer there is a significant rise in the polar/disperse ratio. This means that the heat sealing process is producing polar sites on the surface coating which then contribute to the solid/liquid interaction.

The Kaelble approach to solid liquid interfacial interaction has shown the development of a polar contribution to the surface tension of the solid, and that this arises when the polymeric components are heated. This is very significant when we

consider that the liquids that are to be contained in these carton assemblies are surface active in nature and have a high polar contribution to their surface tensions. The interaction between liquid and solid will therefore be greatest in areas where these polar sites are developed.

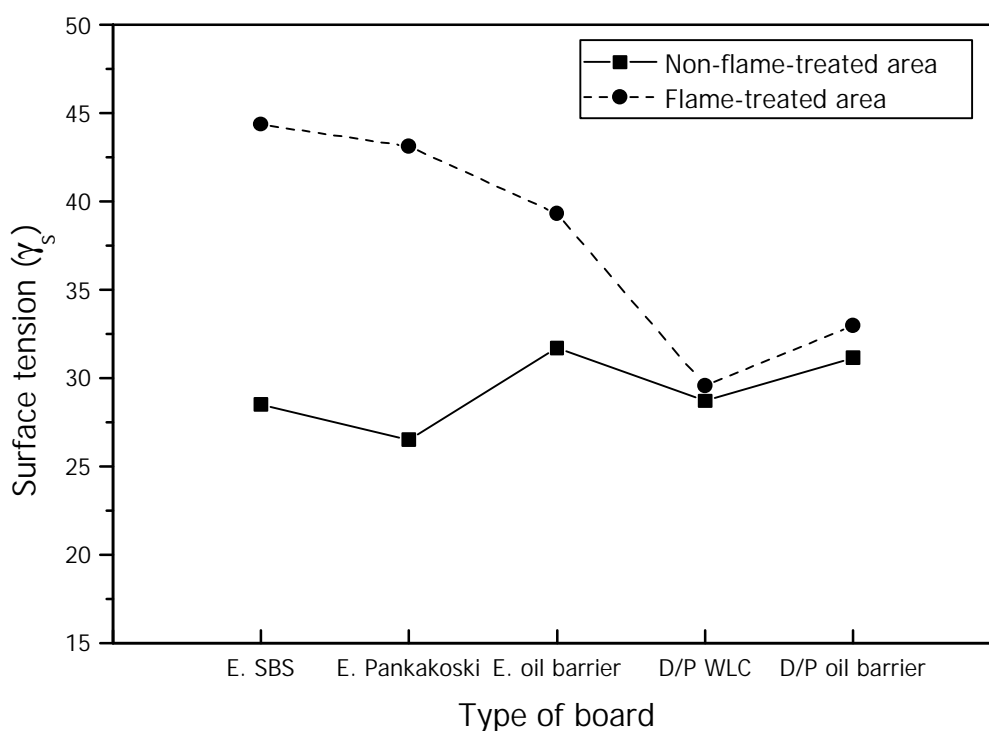
### Thermal Analytical Studies

The polymer coatings that are used in liquid packaging based on carton boards are thermoplastic in nature. Application and subsequent processing of the coatings is reliant on their thermal properties. Therefore, quantification of the thermal nature of these coatings is important.

**Table 5 Surface Tension for Liquids on Polymeric Barrier Coatings – Flame Sealed Areas**

<b>Polymeric barrier coating</b>	<b>Liquid</b>	<b>Contact angle (<math>\theta</math>)</b>	<b>Work of spreading</b>	<b>Cos <math>\theta</math></b>	<b><math>\gamma_s</math></b>	<b>Polar/ Disperse</b>
Enso SBS on flame sealed area	Glycerol	46.3	19.6	0.69	44.37	0.35
	Formamide	40.0	13.6	0.77		
	PEG	26.7	4.8	0.89		
	Tritolyl phosphate	17.6	1.9	0.95		
Enso Pankakoski on flame sealed area	Glycerol	45.6	19.0	0.70	43.13	0.43
	Formamide	42.9	15.6	0.73		
	PEG	30.0	6.0	0.87		
	Tritolyl phosphate	26.9	4.4	0.89		
Enso oil barrier on flame sealed area	Glycerol	52.4	24.7	0.61	39.31	0.23
	Formamide	50.2	21.0	0.64		
	PEG	45.8	13.5	0.70		
	Tritolyl phosphate	26.2	4.2	0.90		
Davidson/ Polycoat wlc on flame sealed area	Glycerol	67.4	39.1	0.38	29.57	0.18
	Formamide	64.2	32.9	0.43		
	PEG	65.5	26.2	0.41		
	Tritolyl phosphate	48.1	13.6	0.67		
Davidson/ polycoat oil barrier on flame sealed areas	Glycerol	69.4	41.1	0.35	32.97	0.12
	Formamide	61.9	30.8	0.47		
	PEG	59.5	22.0	0.51		
	Tritolyl phosphate	41.3	10.2	0.75		

The thermographs arising from differential scanning calorimetric studies of the Enzo SBS, Enzo Pankakoski and Enzo high barrier coatings were very similar and can be represented by Figure 6. Here three thermal transitions are clearly seen. These endothermic transitions occur at 103°C, 125°C and 163°C. In the barrier coating there are two polymer components. These are poly(ethylene) and an ethylene-vinyl alcohol copolymer. The peak centred at 103°C has a base that stretches over about 30°C, the poly(ethylene) beginning to soften at about 90°C.

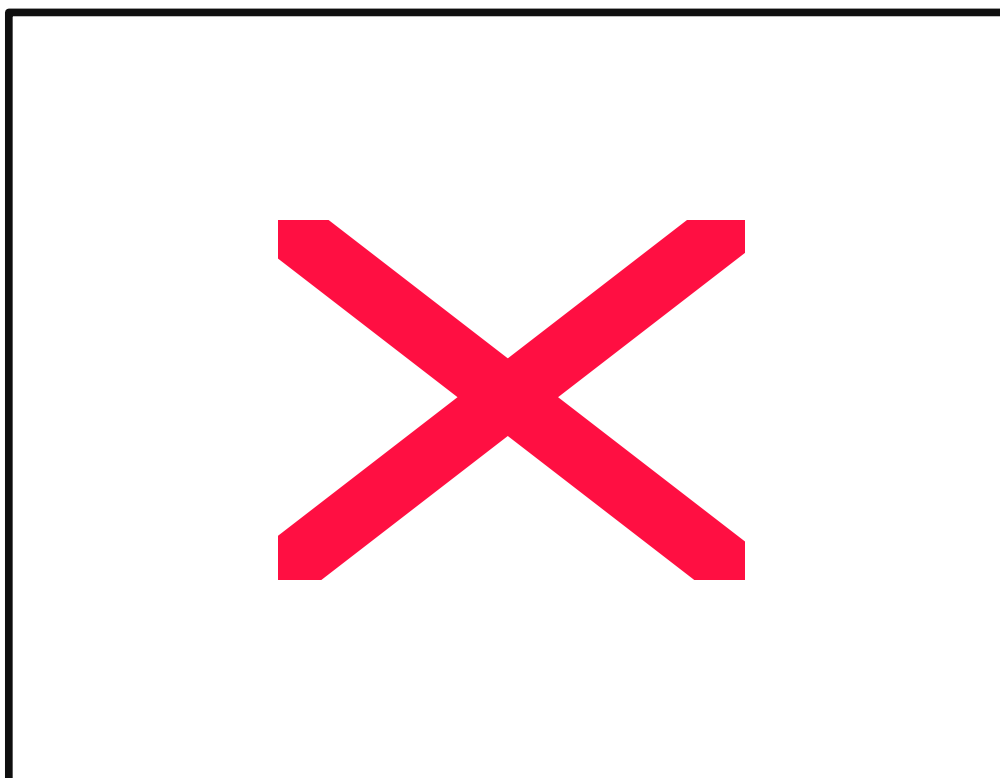


**Figure 5** *Effect of flame-treatment on the surface tension of carton-board*

The thermal transitions of the ethylene-vinyl alcohol copolymer require explanation. The melting temperature for this copolymer is dependent on the percentage of methylene groups in the molten sample. With the methylene group content of about 20%, the melting temperature has been recorded as high as 200°C, with an 80% content, the figure is below 120°C. This information therefore gives us a guide to the results shown in Figure 6. The peak at 163 could be due to the poly(ethylene)/vinyl alcohol copolymer present in the middle of the extrudate. The peak obtained



corresponds to a methylene group content of about 44%. Proprietary extrusion systems have melting temperatures in the range of 164°C-167°C, with methylene contents of approximately 44%, and densities of 1.14g/m<sup>3</sup>. To have good barrier properties ethylene-vinyl alcohol copolymers must have more than 40% of methylene groups in the copolymer.



*Figure 6 Thermograph of Enso standard barrier coating*

### **Particle Size Analysis for Detergent Products**

The particle sizes of the solid matter in colloidal systems such as the detergents that were used in this study are of vital importance when considering physical chemical interactions. The particle size can greatly influence various properties such as diffusion properties, colligative properties, optical properties and flow properties.

The liquid systems being studied provide a broad range of median particle size values from 1 micron up to 20 microns. Although there are similarities between the varying liquids in terms of end use, there are still wide differences in particle size. The liquids

can be identified according to their ability to escape the carton system. They can be classified according to those that pass (containable) and those that fail (not containable). Therefore, non-aggressive liquids will become pass liquids while aggressive and very aggressive liquids will become fail liquids.

Using these criteria in the study of the liquids, 17 liquids are passes while 18 are fails. Of the 18 fails only two have particle size values above 2.25 microns. Of the 17 passes only 5 have particle sizes below 2.25 microns. This infers that a low mean particle size is conducive to carton failure.

### **Solution Characterisation Studies**

Liquid systems that are designed to be contained in carton board assemblies can be characterised in many ways. Certain properties are definitive for a liquid. The viscosity of a liquid is one such property. Many internal and external factors will contribute to a liquid's viscosity. These include the particle size, molecular interactions, solids level, solvent type, density, temperature and so on.

By measuring the viscosity of the liquids and relating the results to other measured parameters, it is possible to obtain a better understanding of the physical chemical nature of the liquid systems. The viscosity of a fluid is a measure of its consistency. It is also a measure of the work spent on maintaining flow or needed to provide flow. The results acquired were converted to the corresponding dynamic viscosity values by division of the capillary values by the density of the particular fluid concerned.

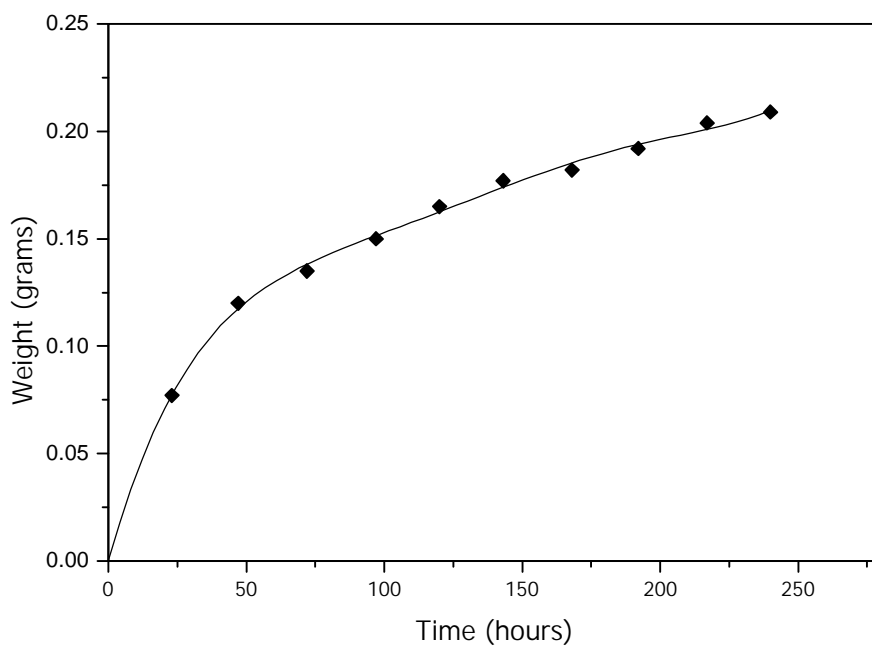
The results represent a wide range of viscosity values from 1 mPas to 7 Pas. The viscosity of the majority of the liquids is between that of water and that of glycerol, whilst some highly viscous liquids have viscosity values which are above that of glycerol. A pattern exists between the viscosity of the liquid and carton integrity failure. Most of the low viscosity liquids are difficult to contain while most of the highly viscous liquids are containable.

### **Wicking Evaluation**

There are two major barriers that a fluid must overcome to escape the carton system. The most effective barrier is the polymer coating that is specifically designed to keep

the liquid product in the carton system. The second barrier is the cellulosic component of the carton-board coupled with the print surface. This is less effective in containing the liquid. This is because the cellulosic component of the carton board acts as an excellent medium for suitable liquids to wick. However, the liquid products do not all wick through the board at the same rate. Clearly, the slower the wicking rate, the more time it will take for the liquid to make the carton unusable. It is suggested that a high wicking rate is a major driving force in pulling the liquid product through any defects in the primary barrier coating and into the carton-board. For this reason, the wicking rates of all the liquid products singled out for evaluation were examined.

Figure 7 gives a typical profile for the weight gained in the wicking study by the identified carton-board, on its exposure to the detergent system over a period of 240 hours. This diffusion rate plot relates to Enzo SBS standard board in contact with a particular fabric conditioner at 20°C.



***Figure 7 Diffusion rate plot for standard 300 g/m<sup>2</sup> paperboard in fabric conditioner at 20°C***

The profiles for a wide range of conditioners and detergents, in conjunction with a range of substrates were very similar. However, the weight gained by the samples

over the 240 hours period varied considerably. For example, the standard board/fabric conditioner combination gave a weight gain value of 0.21g over the 240 hours period. Corresponding values for other board detergent combinations are given in Table 6. The liquids represented in Table 6 portray diffusion rates for the various board types. The three types of liquid highlighted in Table 6 have been chosen to show examples of a containable liquid (N), a semi-containable liquid, (A) and a non-containable liquid, (V). The diffusion plots all exhibited a high rate of weight increase within the first 48 hours. After 48 hours, the rate of weight increase falls as the time period of the experiment increases. The initial spurt is probably due to a high concentration differential between the liquid and the carton board in the first 48 hours. The concentration of liquid within the carton board will be zero at time zero. There will be a stronger driving force as the liquid travels from a high concentration zone to a low concentration zone. As the experiment progresses, the concentration differential at the liquid carton board interface decreases and the rate of diffusion will also be reduced correspondingly. Some fluids wick to an appreciable extent and do so quickly. Others wick to the same extent, but significantly more slowly. Some liquids wick to a limited extent only, but do so rapidly. Other liquids wick to a limited extent and do so slowly.

<i>Table 6 Diffusion Extent from Wicking Studies</i>			
<b>Wicking status of fluid</b>	<b>g of fluid wicking/240 hours</b>	<b>g of fluid wicking/20 hours</b>	<b>Mass ratio (240/20)</b>
N	0.21	0.06	3.5
N	0.36	0.09	4.0
A	0.41	0.10	4.0
A	0.54	0.13	4.1
N	0.63	0.20	3.15
V	0.69	0.18	3.83
V	0.98	0.40	2.45
A	1.01	0.18	5.61
V	1.18	0.50	2.36

The liquids wicking through the various carton boards are complex mixtures of colloidal particles and dispersion media. The board sample performs chromatographic separation on the liquids as the various components wick at different rates. The larger or heavier particles will wick more slowly through the board, while the faster moving solvent components will be at the front of the diffusing liquid. This was observed, during the experimental measurements, by the occurrence of colour separation, of the coloured liquids, within the board structure. The liquids exhibited colour separation with coloured particulates moving slowly behind the solvent front of the liquid. This may also explain the reduction in diffusion rate as the experiment progressed.

Differences in wicking rates are also evident between different board samples. It would therefore appear that the liquids are able to penetrate boards made from recycled grade pulps to a greater extent than applies to boards made from virgin pulps. This may be due to the degree of fibre compression leading to a reduced number of voids in the board structure, or due to the level of swelling in the board.

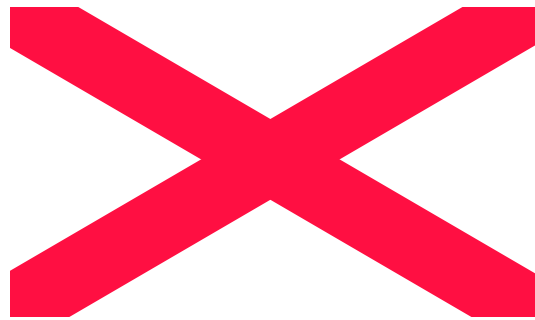
Several test liquids were chosen to represent a sample of semi-containable liquids and non-containable liquids in a study of the effect of temperature variation on containment. Figure 8 gives plots produced from these temperature studies. The weight gain increases significantly as the conditioning temperature increases. The greatest increase of weight gain is seen above 40°C. The gains at 20°C and 30°C are only marginally different.

This temperature/wicking plot also shows that as the temperature is increased, the time to reach saturation decreases. At 50°C a saturation point is reached within 120 hours at 60°C the time taken is only 50 hours.

The temperature study shows that wicking is dependent on temperature. If carton failure is influenced by liquid wicking ability, then it is likely that heat input influences the rate of carton failure. From Figure 8 we can say that a doubling of the temperature from 20–40°C causes the weight gain to quadruple. The effect of temperature on the rate of wicking is likely the result of a combination of factors including the change of physical chemical characteristics, such a surface tension and kinetic viscosity of both the board material and the containment fluid.

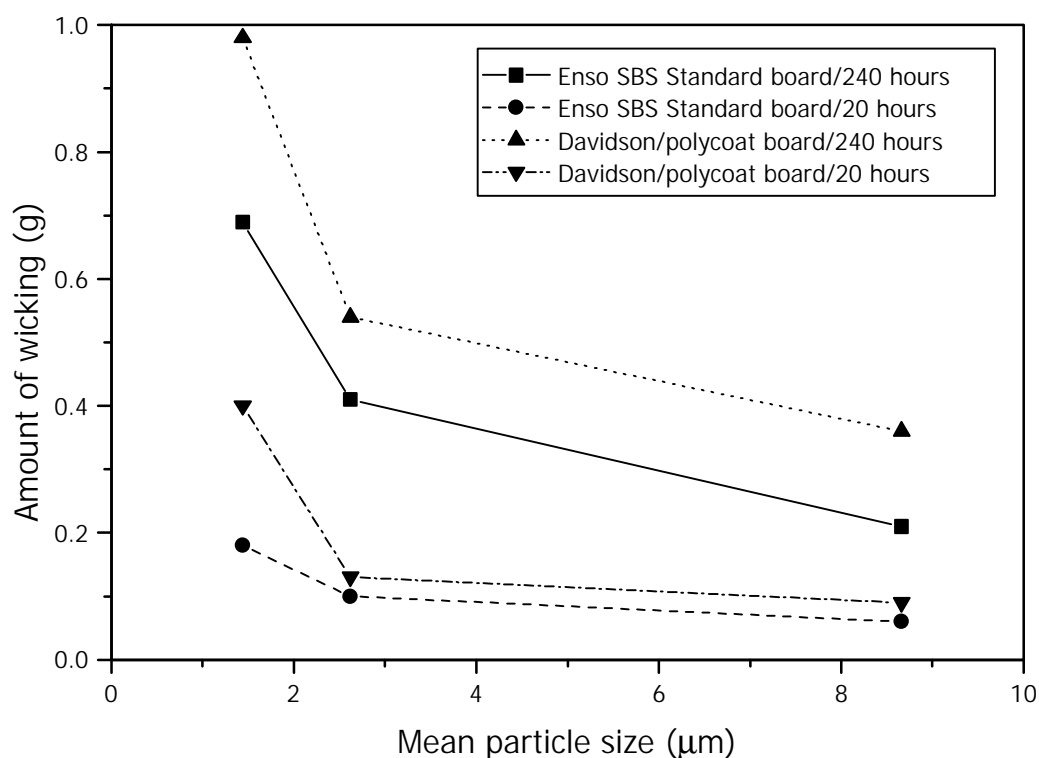
This study has shown that for the majority of liquids, the higher the ability to wick through the carton board, the more likely it is that carton failure will occur. Heat input greatly influences wicking rates.

The dependence of the rate of wicking on the mean particle size of the containment can be seen from Figure 9. Thus, generally speaking, the larger the mean particle size the lower the rate of wicking will be.



*Figure 8 Diffusion rate plot for Enso SBS standard 300 g/m<sup>2</sup> paperboard in Henkel HDL – temperature study*

Clearly, the rate of wicking is also dependent on other physical chemical characteristics of both the carton-board and the containment fluid. In terms of the containment fluid, these characteristics include the kinetic viscosity, the density, the surface tension and the particle size and particle size distribution. Results obtained in this study have indicated that, in most cases, the particle size, particle size distribution and surface tension have more significant effect than the density and the kinetic viscosity.



*Figure 9 Dependence of wicking on the mean particle size of the containment*

### **General Summary**

Several general properties of liquid systems were measured to examine the fundamental nature of such systems. The processes involved in containment failure are varied and complex. The physical chemical properties of the commercial liquid systems have been shown to influence containment. The characteristics of containment failure are such that several physical chemical properties will influence the magnitude and speed of failure. Liquids designed for similar applications have been shown to have different characteristics. Thus, attempts at failure prediction must be carried out with care. Specific properties influencing failure may vary from liquid to liquid. This study has been concerned with commercial liquid products. Due to the nature of the liquid-packaging industry, information on the specific composition of a contained liquid is usually difficult to acquire. For this reason, the study has emphasised general physical chemical properties relating to total liquid formulation, rather than specific properties of individual components.

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