EXTENDED ABSTRACT
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Evaporated aluminium on polyester: optical, electrical, and barrier properties as a function of thickness and time (Part I)
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Abstract

We have produced aluminium films on polyester at various thicknesses using a high speed, industrial roll-to-roll metallizer and characterized them using a range of methods. This work is presented in two papers. For this first paper, we have measured the optical, electrical, and barrier properties for each sample as a function of aluminium film thickness and time. We have also measured the variation in the optical density as a function of down web and cross web position on the substrate. The films were produced in thicknesses corresponding to optical densities of approximately 0.5 to 2.5 in 0.5 OD steps which corresponds to physical thicknesses of about 6-40 nm. A companion paper (Part II) will describe a suite of analytical measurements to characterize the film thicknesses and will discuss the utility of film thickness in predicting the optical and electrical properties of the films.

Introduction

For several decades, aluminium thin films have been successfully deposited on various polymer base substrates for the following applications:-

- Light protection (Including UV)
- Barrier protection (WVTR, OTR, CO2, Aroma/ flavour)
- Reflection/ absorption requirements (Optical - Solar/ window film)
- Improvements in aesthetic appeal
- Low energy requirements (Electrical - Conductive tracks/ capacitors)

To date, the largest volume market for aluminium metallized polymer films is for packaging applications where a number of the above features are required. Packaging has proven essential to prevent product losses in storage, distribution and the preservation of food, etc. Correctly engineered packaging has virtually eliminated the risk of contamination of foodstuffs by microorganisms.

The preservation of foodstuffs is achieved by the inherent design of the packaging structure, whose primary function is to provide optimised barrier performance to extend the shelf life of the product it's protecting. Barriers to gases and light are essential depending on the packaging application. Historically, these barrier properties were achieved with aluminium foil, aluminium foil/paper laminates and multi laminated films. These barrier materials were not ideal due to the high-energy content of the aluminium foil production and the mass of material employed.

Substitution technologies were investigated with the intention of reducing the economical and environmental implications of the traditional packaging structures, and vacuum metallizing became a viable substitution technology to deposit thin 'nanometer' metal coatings onto polymeric substrates. The physical vapour deposition technique works by vaporizing the metal in a vacuum chamber and allowing the metal to condense onto the passing substrate. The integrity of this extremely thin metal layer was found to provide excellent barrier to light, water vapour, oxygen as well as other gases and aromas.

The extremely thin layer of metallized coating of only 0.00005 mm thickness offers the highest yield per m^2 compared with other barrier materials. For example: 1 kg of pure aluminium gives 41 m^2 of aluminium foil (0.009 mm) whereas a metallized surface gives 5000 m^2. A resource preservation ratio of 1:125! [1]

The 'clean' metallizing process requires a minimal amount of energy when compared to products offering similar properties. To produce a layer of 0.05 g/m^2 requires only 92 kJ (industry average) including the energy used for the production of the aluminium itself. Compared to the production of 20-24 g/m^2 of aluminium foil, an energy saving of more than 97 % is achieved. Metallized materials, therefore, offer a substantial reduction of waste in packaging since monolayers can be used to replace multi-layer constructions. Metallizing provides the lowest level of surface metal deposition compared to all other forms of metallic surfaces. When applied onto a single web of film, paper or board, the metallized substrate can be considered effectively as a monolayer structure and recycling poses no problems. Monolayer films can be re-granulated whilst paper and board can be re-pulped and reused [2].

Based on the above, the thermal vacuum evaporation of aluminium onto polymer films has become a standard technique and such films are used widely for food packaging and decorative, reflective and other technical applications. For food packaging the gas permeation is the most important property. In order to maintain a high shelf life for a given content, a high barrier against oxygen and/or water vapour permeation is necessary. Polyester or polyethylene terephthalate (PET) and biaxially oriented polypropylene (OPP) are the most widely used film types for such an application. This paper will focus on the thermal evaporation of aluminium on a PET base substrate and will try to characterise the optical, electrical and barrier properties of the thin film and the coated material.

When considering barrier performance, numerous hypotheses have been put forward to explain the lack of a "perfect" gas barrier for metallized polymer films: these include pinhole formation during crystallization of the aluminium layer, or interfacial roughness caused by anti-blocking particles in the polymer surface. Clearly, the physicochemical nature of the metal/polymer interface is of prime importance [3].

In order to provide an indication of the size of the market for metallized film, in 2005 the total market for metallized films was estimated at 25 billion m^2 worldwide, or 400,000 tons per annum [4], with a growth of 4-6 % per annum.

Metal Thickness – Why do people care about metal thickness versus optical density?
When trying to determine the quality level of aluminium metallized films for lower cost commodity packaging applications (single layer, not the final laminated structure), the industry has generally standardised on using optical density (OD) as the accepted quantitative measurement. From the optical density measurements obtained, assumptions are generally made regarding metal thickness and/or the general barrier expectations for the metal film. Determining the optical density and obtaining statistical data to show the cross web and down web uniformity is a relatively simple, low cost technique, and one which can be obtained directly from the metallizer itself, via the in-line monitor systems that generally exist on the more modern vacuum roll coaters. Off-line comparison measurements can also be taken, and the associated equipment costs of the off-line densitometer together with the time taken to create the measurements provide an economically viable solution, which provides some level of quality assurance for the coated material. If the need arises, look up curves are generally used to obtain metal thickness and barrier data for a given OD level. Barrier and thickness data is now available for different base substrates with varying surface roughness and polarity levels, and even plasma treated and untreated surfaces conditions are covered. A common reference tool used in the industry to translate OD to metal thickness is from the data given by Scharr industries or Advanced Ceramics Corporation, which is published in the Aimcal technical reference manual and is shown in Fig 1.0 below.
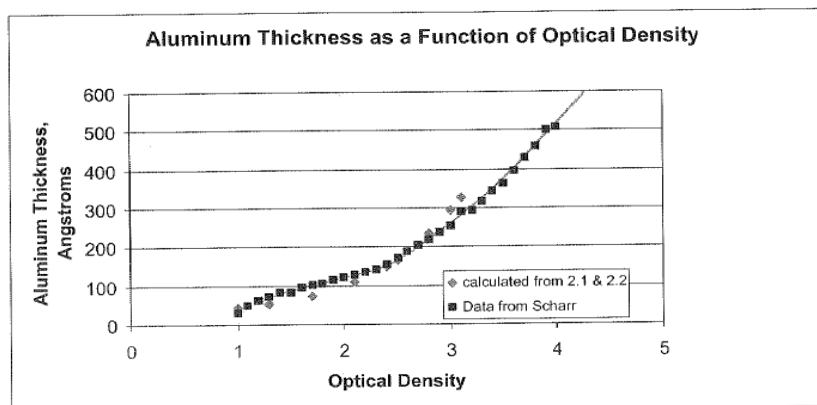

Fig 1.0 Comparison of calculated aluminium thickness vs. optical density

A source of error with using the above graph is the phenomenon that exists when the high purity aluminium thin film is exposed to atmospheric conditions and oxidation of the layer results. In creating the partially oxidised material, the optical properties of the thin film change by increasing the visible light transmission through the film, decreasing the optical density of the film (OD = Log_{10} (1/ Light transmission)) and increasing the associated coating mass and relative thickness via the oxygen absorption or 'gettering' process.

Aluminium is a reactive metal, which readily oxidizes in air to form a stable surface oxide 30 and 50 angstroms thick. This barrier layer protects the underlying metal from further chemical attack as a result of its high electrical resistivity, which hinders the electron flow required for $O_2 + 4e^- \rightarrow 2O^{2--}$ reaction. At ambient temperatures, growth of an amorphous oxide layer takes place at the metal surface, which readily hydrates to form aluminium oxide hydroxides (AlO(OH)) or hydroxides ($Al(OH)_3$) [5].

Based on this oxidation phenomenon, thickness determination via light transmission measurements is found to be very time dependent post metallizer, and therefore only when a stable oxidised layer protecting the aluminium thin film is obtained, can reference to physical thickness be made via optical density determination.

As OD measurements basically determine the amount of light transmission through the coated material, they also include absorption/ reflection losses of the base material, and unless the user of the densitometer subtracts the base film light transmission off the total transmission value, an error or variance based on the base film will be present. Generally speaking, a plain packaging grade 12 micron PET has a LT and OD of 91.20 % and 0.04 OD respectively, whereas a 20 micron OPP has more optical clarity with an LT of 93.33 % or 0.03 OD. Higher cost optical grade films have been developed with a higher degree of optical clarity but for packaging applications these would not be economical viable. Although the OD of the base substrate is generally low in comparison with the deposited material it should not be discounted and for thinner solar or susceptor type coating it can introduce more error.

Another problem when using light transmission to measure film properties is that measurements tend to be averaged over the measurement area (typically 7 to 20 mm^2). When considering metal thicknesses in the low nanometer range, thickness can vary significantly over a mm range based on a number of potential causes from surface polarity/ energy differences, surface roughness, protruding anti-block additives, pin holes via spitting, pick-off due to blocking. We therefore cannot accurately determine coating thickness via standard densitometer measurements unless it is used as a qualitative guide.

Sheet resistance is another industry adopted measurement technique to determine quality, coating uniformity, optical density and is sometimes linked to metal thickness associated barrier levels of the material. Unlike optical transmission measurements, sheet resistance is a measurement of the thin film only and therefore is not affected by variation in optical transmission/ absorption of the associated polymer carrier. Like OD measurements, sheet resistance of the vapour deposited material can be obtained via an in-line non-contact measurement system on the metallizer. For resistance measurements, the in-line monitor system uses an eddy current system whereas for optical density an optical transmissive system is adopted. For both monitor systems user input graphs can be created to allow the metallizer to use an OD and resistance set point. For off-line measurements a resistance monitor (simple hand held device or a more accurate four point probe) is used. Like optical density, sheet resistance is also affected by oxidation as sub-stoichiometric aluminium oxide can have a very high dielectric strength, which may dilute the bulk resistivity of the thin film. For a given deposition rate onto the passing polymer the sheet resistance is affected by a number of factors including vacuum level, atmospheric conditions (temperature and humidity) post machine, material surface, additives used and also plasma treatment, which again complicates matters. As sheet resistance is an area measurement and not a volume measurement, it is important to measure at a depth in the coating where surface oxidation does not affect the true electrical properties of the bulk material.

There is a perception in the industry that metal thickness and even barrier is directly related to optical density, and several studies have been carried out over the years to evaluate if such a relationship existed. Repeatedly this has proven not to be the case, and the relationship is very much condition specific. Several studies have shown that for a given thickness of aluminium the barrier properties and optical properties of the film can be drastically affected by a number of variables, including: - Fractional pin holes, surface polarity, surface roughness and more importantly, level of oxidation of the thin film. Rather than increasing the thickness of the deposited layer, which is commonly used in the industry to improve the barrier performance of the coated film, it may prove more productive to understand and resolve the parameters which directly affect barrier performance and maintain a more optimised reduced defect aluminium layer.

"*The amount of metal deposited on the surface of a film will govern the oxygen (O$_2$), water vapour transmission (WVTR), and light barrier properties of that film. Hence a method to measure this coating is needed so that one can determine the amount of metal that will meet a particular requirement*" [6].

From a metallizer manufacturer's perspective an accurate determination of the coating thickness along with the associated coating mass density is used to determine the collection efficiency of the metallizer. This is often used as an important differentiator or selling feature between metallizer suppliers, which is, based upon the different source geometry, coating aperture sizes, source to film distance and vacuum levels achieved. Accurate industry standard thickness vs. OD data is essential to make this comparison.

For applications where control of light ingress or UV protection is required, optical absorption/ reflection/ transmission measurements are more important than thickness as this is more critical than understanding the physical coating thickness of the deposited material. A thick fully transparent oxide coating will obviously not provide the same level of light barrier as a thinner aluminium sample and therefore optical methods are the selected option for determining the effectiveness of a thin film against light ingress. Again based on the time dependence of the optical properties, it is essential ageing measurements are recorded to fully characterise the change in optical properties over time.

New technologies for the surface treatment of polymer films in the metallizing chamber have shown the sheet resistance of the thin film, at a fixed aluminium deposition rate, will depend upon the surface treatment level of film. Thus, for a particular metallized film product, the process used to make it will determine the ultimate properties of the aluminium layer deposited, based upon the thickness and density of the aluminium and any other interfacial effects which might be important. From this, it can be seen that it is unlikely that a unique relationship will exist for the optical vs. barrier properties of a film for OPP where the metallized surface may have many compositions [7].

Description of the metallizer platform

The machine platform used for the metal thickness trials was a 2007 General Vacuum Equipment K4000 vacuum roll-to-roll coater with a thermal resistive PVD source. The machine had a maximum effective coating width of 1650 mm and can accommodate roll diameters of up to 1000 mm. The maximum line speed of the machine was 840 m/min.
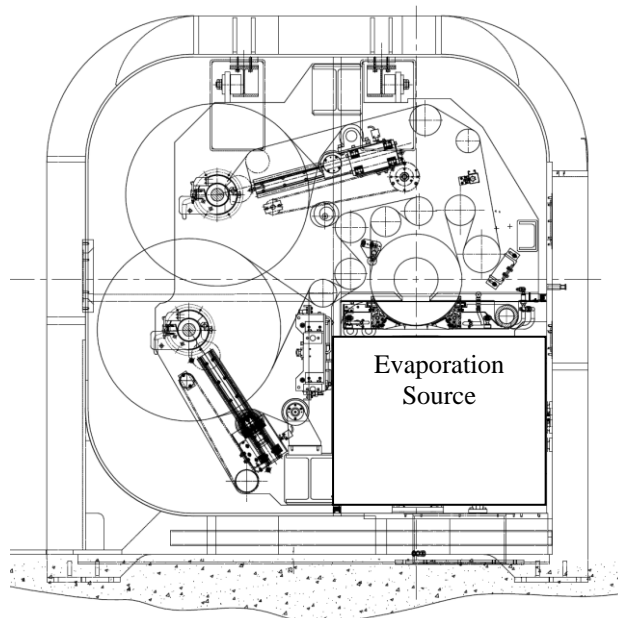

Fig 2.0 A schematic to illustrate the vacuum roll coater used to create the metallized samples

The vacuum chamber had two separately pumped zones, which operated at two different pressure regimes, namely the winding zone and the evaporation zone. The pumping group for the winding zone consisted of a two stage mechanical blower system (12865 m^3/hr and a 4035 m^3/hr) backed by a variable pitched screw dry pump with a pumping speed of 630 m^3/hr, and the evaporation zone is pumped by 3 x 10,000 lpm diffusion pumps backed with a 4035 m^3/hr mechanical blower and a further 630 m^3/hr screw dry pump. A polycold fast cycle water vapour cyro pump is also employed in the evaporation zone with a theoretical pumping speed of up to 300,000 l/sec.

Pressure measurements on the machine were achieved with the aid of a micro pirani thermal conductivity gauge in the winding zone, and both micro pirani and penning cold cathode ionisation gauges in the evaporation zone.

The winding system consisted of four digital a.c vector drives, which permitted separate adjustment of the winder stations, process drum and capstan draw roller, and various spreader rolls were used at key positions in the winding mechanism.

The thermal resistive evaporation source used standard IMC (inter-metallic compound) evaporator boats and these were arranged in-line with a pitch of 100 mm. Individual thyristor controlled transformers are employed for precise control of the power delivered to each of the evaporator boats and individual stepper motors drives are used for precise control of the wire feed rate to each evaporator.

During web coating, a special multi point optical transmission monitor system continuously samples the aluminium deposit at regular intervals across the web width. The data is fed back to the computer control system, which automatically adjusts the wire feed rate and power delivered to the evaporators to maintain the desired deposition level.

To prevent thermal damage to the polymer substrates in the deposition zone, the film is supported on a large diameter water-cooled process drum with capabilities of being chilled to -20 °C, which minimises the thermal load from the radiant and condensable heat from the aluminium vapour cloud. A gas wedge injection system further enhances the heat transfer by injecting higher-pressure localised gas with a lower mean free path between the process drum and the web.

The machine was fitted with an optional in-line plasma treatment device; although, this was not used for the purpose of the metal thickness trials as it was considered a further variable which could complicate the basic physics behind the standard aluminium metallizing process.

Based on the gas cloud interaction, which exists with an in-line source configuration pitched at 100 mm increments, removable shielding is employed to selectively mask deposition differences between 'over' and 'between' the evaporator boat positions. For low deposition levels or wire feed rates with a more open and lower pressure gas cloud, the aperture masking is not required. For higher deposition rates, shaped shields can be fitted on one or two sides of the aperture window.

Coating trials conducted:-

Five initial coating trials were conducted on a 12 micron corona treated polyethylene terephthalate base substrate varying the wire feed rate to obtain the required optical density levels. The trial set is summarised in table 1.0 below:-

OD Target*	0.5	1.0	1.5	2.0	2.5
Line Speed (m/min)	475	510	420	380	380
Wire Feed Rate (g/min)	2.14	4.02	4.96	6.16	7.10
Evaporation Zone Vacuum Level (x 10^{-4} mbar)	2.8	3.9	3.2	6.9	8.4
Source Masking	None	None	None	Present	Present
Gas Wedge Gas Feed (SLM)	1	1	1	1	2.5

Table 1.0 a table to illustrate the various coating trials conducted

Notes:
* The OD target includes both the deposited aluminium thin film and the base substrate

For the coating trials conducted, the process drum was operated at -15 °C and, with the exception of the 2.5 OD trial, a gas wedge volumetric gas flow of 1 SLM of atmospheric air was used. To prevent wrinkling/ tram-lining of the material when exposed to the heat load from the source, the gas flow had to be increased to 2.5 SLM for the 2.5 OD coating trial.

The polyester film used for the trials was type MAD-xy supplied from Shaoxing xiangyu green packaging Co. Ltd in China, which had a minimum surface tension level of 58 mN/m. To help reduce the number of potential variables involved in the study, all trials were conducted on the same input roll and done consecutively without breaking vacuum.

The aluminium wire used for the trials was 2 mm diameter EN-AW-1080 supplied by Manfisa, Italy and had a minimum aluminium content of 99.8 %. A density of 2700 kg/m^3 was used to determine the wire feed rate.

The evaporator boats used were standard rectangular section 2 component boats supplied by Kennametal Sintec Keramik GmbH and had a hot resistivity of 2800-3200 μ Ω cm.

Optical Density Measurements

OD measurements were taken in the vacuum roll coater using an in-line non-contact optical monitor using a 5 mm spot size at 626 nm wavelength designed by General Vacuum Equipment Ltd. Sender and receiver pitching was set to 100 mm and positioned in-line above each evaporator boat.

With the in-line optical monitor calibrated with a certified lens, the coating trials on the machine were conducted in open loop control and the wire feed rate was manually adjusted to achieve the desired OD target level, namely 0.5, 1.0, 1.5, 2.0 and 2.5 OD. A static fully oxidised reference sample of coated film was also positioned in the measuring width of the beam to ensure the OD levels obtained were accurate during processing and didn't drift with time, vacuum or temperature variations.

In order to measure the optical density levels of the metallized samples out of the metallizer, an off-line bench top Macbeth 931 transmissive densitometer with an orthochromatic response was used. The peak sensitivity is at 510 nm and a 50 nm band of wavelength around this peak sensitivity accounts for 38 % of the total sensitivity.

The on-line transmission beam used for the trials operates at a wavelength of 626 nm whereas the off-line densitometer follows more of an ortho spectral response from 380 nm to 610 nm with a peak sensitivity at 510 nm (520 nm +/- 25 nm represents 38 % of the total sensitivity). Therefore, a user created red shift curve was used on the metallizer to account for the offset in optical measurements obtained between the two systems, and this needs to be plotted across the full operating optical density range required for the products to be metallized. The red shift offset curve has been found to be product specific and therefore an individual user defined curve can be created with each process recipe on the machine. As the offset varies at different OD levels, a large amount of trials need to conducted for each product in order to create an accurate curve fit. For the purpose of the trials, the red shift values tabulated in Table 2.0 below were used.

*Target on machine OD	0.5	1.0	1.5	2.0	2.5
Red Shift Offset	0.2	0.25	0.3	0.3	0.35
Set Point without Red Shift applied	0.7	1.25	1.80	2.30	2.85

Table 2.0 a table to illustrate the red shift values used for the on-line optical beam

A base measurement of the un-metallized PET was taken and found to be 0.04 OD or (91.20 % LT) and this should be deducted from the overall measurement to give the metal only optical density if required.

Measurements of OD and resistivity were made in both the machine (MD) and transverse direction (TD) on a centrally cut swatch from the finished roll measuring 24" x 24". The results consisted of 36 measurements per trial evenly spaced in both the MD and TD over the 576"^{2} area of the metallized sample.

The off-line optical density measurements obtained for the various coating trials conducted are tabulated in Table 3.0 and 4.0 below and represent the optical density of both the PET base substrate and the aluminium thin film following an off machine time period of 5 and 221 days respectively.

Statistical Analysis of the Optical Density Results – 5 days aged

Statistical Analysis	Optical Density				
	0.5OD	1.0OD	1.5OD	2.0OD	2.5OD
Mean	0.41	0.92	1.47	1.95	2.58
Standard Error	0.002	0.002	0.004	0.004	0.009
Median	0.40	0.92	1.48	1.95	2.59
Mode	0.40	0.92	1.48	1.95	2.59
Standard Deviation	0.012	0.012	0.022	0.026	0.052

Sample Variance	0.000	0.000	0.000	0.001	0.003
Kurtosis	-1.00	-0.30	-1.06	0.18	-0.94
Skewness	0.61	0.59	-0.31	0.06	-0.02
Range	0.04	0.05	0.08	0.11	0.18
Minimum	0.4	0.9	1.4	1.9	2.5
Maximum	0.4	1.0	1.5	2.0	2.7
Sum	15	33	53	70	93
Count	36	36	36	36	36
Confid. Level (95 %)	0.004	0.004	0.007	0.009	0.018
MD Average Std Dev	0.0036	0.0041	0.0073	0.0075	0.0123
TD Average Std Dev	0.0125	0.0132	0.0233	0.0264	0.0555

Table 3.0 a table to illustrate the OD measurements and statistical data for the 5 days aged samples

From the results obtained, we can observe more variation in the TD OD levels compared to the MD levels. The increase in OD variation is thought to exist due to a more significant change in deposition levels based on the varying interaction of the aluminium vapour clouds across the width of the machine. Whereas, the variation in the MD direction is more to do with changes over time and this shows the deposition rate per time is constant over the measurements taken. Average STD Dev for all measurements taken in the machine direction was found to be 0.00546 (n = 180) opposed to 0.02618 for the sample number in the transverse direction.

Statistical Analysis of Optical Density Results – 221 days aged

Statistical Analysis	Optical Density				
	0.5OD	1.0OD	1.5OD	2.0OD	2.5OD
Mean	0.38	0.89	1.41	1.91	2.49
Standard Error	0.002	0.002	0.004	0.007	0.006
Median	0.38	0.89	1.42	1.91	2.50
Mode	0.37	0.89	1.42	1.90	2.50
Standard Deviation	0.010	0.013	0.021	0.041	0.036
Sample Variance	0.000	0.000	0.000	0.002	0.001
Kurtosis	-1.41	-0.09	-0.44	-0.80	-0.61
Skewness	0.10	0.74	-0.59	-0.36	-0.39
Range	0.03	0.05	0.07	0.14	0.13
Minimum	0.4	0.9	1.4	1.8	2.4
Maximum	0.4	0.9	1.4	2.0	2.6
Sum	14	32	51	69	90
Count	36	36	36	36	36
Confid. Level (95 %)	0.003	0.004	0.007	0.014	0.012

Table 4.0 a table to illustrate the OD measurements and statistical data for the 221 days aged samples

Summary table to show the OD oxidation/ degradation for the various trials conducted

Condition	Optical Density (OD)/LT (%)				
Base Film	0.04 (91.20)	0.04 (91.20)	0.04 (91.20)	0.04 (91.20)	0.04 (91.20)
On Machine OD Target	0.5 (31.62)	1.0 (10.0)	1.5 (3.16)	2.0 (1.00)	2.5 (0.32)
Post Machine OD (5 days)	0.41 (38.90)	0.92 (12.02)	1.47 (3.39)	1.95 (1.12)	2.58 (0.26)
Post Machine OD (221 days)	0.38 (41.69)	0.89 (12.88)	1.41 (3.89)	1.91 (1.23)	2.49 (0.32)
Overall Reduction in OD**	0.12 (75.86)	0.11 (77.62)	0.09 (81.28)	0.09 (81.28)	0.01* (81.28)
Reduction in OD post machine	0.03 (93.33)	0.03 (93.33)	0.06 (87.10)	0.04** (91.20)	0.09 (81.28)

Table 5.0 a table to illustrate the OD measurements over time and associated oxidation

* The overall reduction in OD for the 2.5 OD trial shows a reduction of 0.01 OD after a time period of 221 days from the machine. This appears extremely low based on the other data and one potential explanation of this would be the red shift curve at the higher OD level may be inaccurate and may need re-checking. The fact that the 5-day post machine partially oxidised sample measured a higher value at 2.58 suggests the OD on the machine must have been higher and again reconfirms the red shift curve may need to be increased at this higher OD level.

** The reduction in OD post machine removes any error related to red shift and therefore you would expect a relationship to exist between the quantity of aluminium deposited on the polymer carrier and the reduction in OD over time. An increase in OD reduction was found from the 0.5 OD sample through to the 2.5 OD sample, with the exception of the 2.0 OD sample where a much lower reduction in OD was found over a constant post machine time or ageing interval.

In summary the largest change in OD was recorded between 0 to 5 days and this suggests further trials mapping the short term OD change with an increase in associated data points is required.

Graphical Analysis of Resistivity and Optical Density Results – 5 & 221 days aged samples

Previous studies have characterised the relationship between sheet resistance and optical density on an aluminium metallized polymer structure, and simplistically as more metal was deposited the transparency of the film reduced, whilst the conductivity of the thin film increased. However, changes in the optical properties of the film can also result from oxidation of the reactive aluminium layer when it is exposed to an oxidising atmosphere, and it was found that a decrease in optical density (more transparent) and an increase in sheet resistance (less conductive) resulted. In order to illustrate the relationship between optical density and sheet resistance with an added time factor, the graph shown in Fig 3.0 below was created. The graph contains 360 data points at 5 days and 221 days post machine intervals.
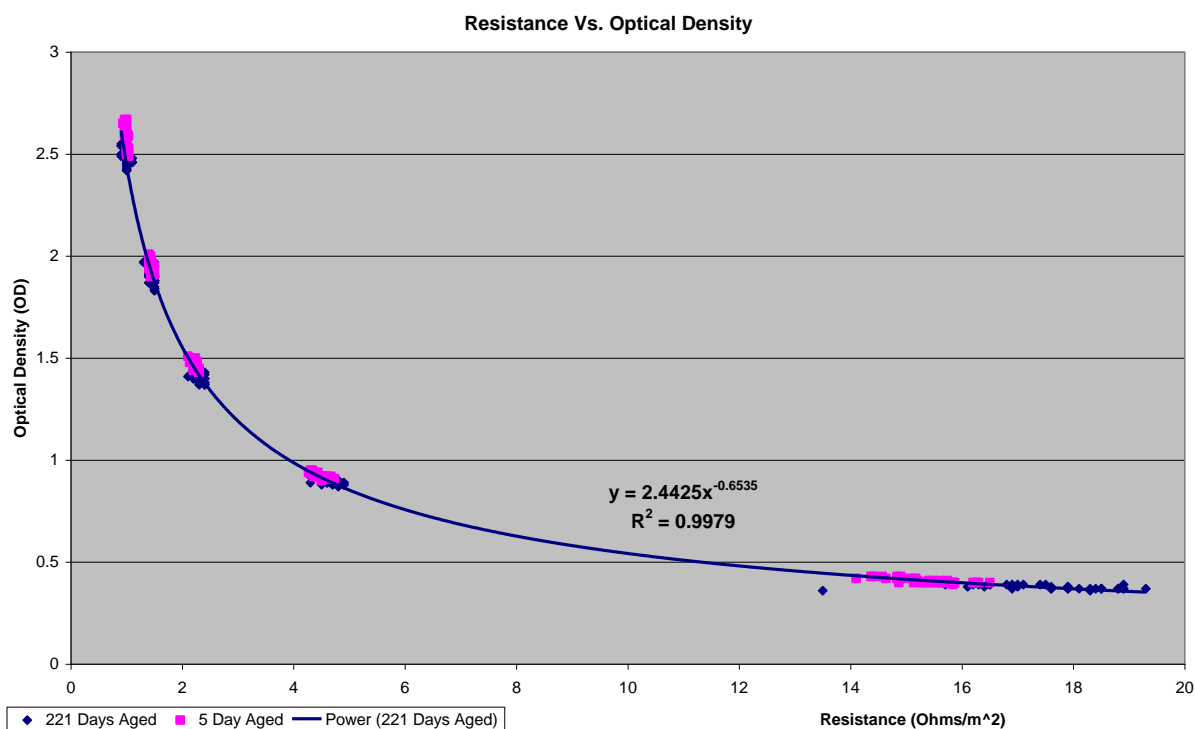

Fig 3.0 – A graph to illustrate the relationship between optical density, sheet resistance and oxidation on 12 micron PET

Even though phenomenon of oxidation was found to change the optical density of the coated films over time, it was also found the oxide surface altered the sheet resistivity of the film, and a very good correlation was found between the measured OD of the film and the sheet resistance. Regression of the data yields the following polynomial curve:-

$$Y = 2.4425(X)^{-0.6535} \qquad R^2 = 0.9979$$

Where:-

Y = Optical Density (OD)
X = Resistance (Ω/□)

The graph above suggests that a critical thickness of aluminium/ aluminium oxide is required (approx 18-25 nm or 1.5 OD) prior to obtaining good electrical continuity in the thin film, and once that has been achieved a more significant increase in conductivity per optical change occurs which can be shown in the 1.5 to 2.5 OD range.

Short Term Oxidation
Metallized polymer films are widely used for gas barrier applications, xerography, composites, and photoconductive materials. Aluminium is often employed in this context; it is a reactive metal, which readily oxidizes in air to form a stable surface oxide (thicknesses between 30 and 50 angstroms). This barrier layer protects the underlying metal from further chemical attack as a result of its high electrical resistivity, which hinders the electron flow required for $O_2 + 4e^- \rightarrow 2O^{2-}$ reaction. At ambient temperatures, growth of an amorphous oxide layer takes place at the metal surface, which readily hydrates to form aluminium oxide hydroxides (AlO(OH)) or hydroxides (Al(OH)$_3$) [8].

In order to characterise the rate of oxidation, two further process trials were conducted at different deposition rates to provide 0.5 and 2.2 OD. An additional plasma pre-treatment trial was added, with the change in optical density being recorded over a time period. As aluminium readily oxidises in the presence of air, the time increments selected for the measurements were selected to focus more on the short-term oxidation effects of the deposited thin film. The short-term oxidation curves are detailed in Fig 4.0 and 5.0 below

The first measurement obtained was taken immediately after the deposition phase inside the vacuum roll coater using a General Vacuum Equipment in-line optical monitor using a 5mm spot size at 626 nm wavelength with a reference sample used in the width of measurement. The second measurement taken was immediately after venting and opening the machine using the off-line optical densitometer described above. All subsequent measurements were taken at the various times referenced below and with the samples stored in a laboratory with ambient conditions of 19-20 °C and 50-60 % RH. The reduction in OD v's time for the 0.5 and 2.2 OD sample is shown in the Fig 4.0 and 5.0 respectively below.
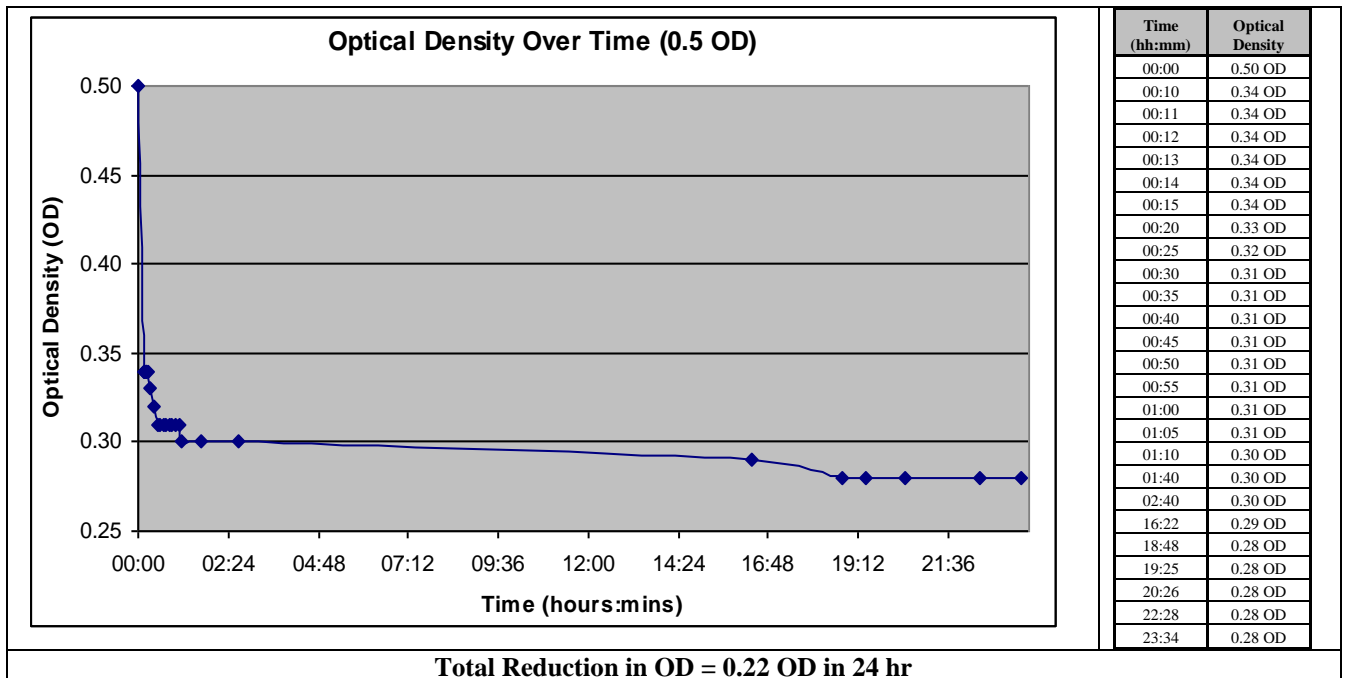

Time (hh:mm)	Optical Density
00:00	0.50 OD
00:10	0.34 OD
00:11	0.34 OD
00:12	0.34 OD
00:13	0.34 OD
00:14	0.34 OD
00:15	0.34 OD
00:20	0.33 OD
00:25	0.32 OD
00:30	0.31 OD
00:35	0.31 OD
00:40	0.31 OD
00:45	0.31 OD
00:50	0.31 OD
00:55	0.31 OD
01:00	0.31 OD
01:05	0.31 OD
01:10	0.30 OD
01:40	0.30 OD
02:40	0.30 OD
16:22	0.29 OD
18:48	0.28 OD
19:25	0.28 OD
20:26	0.28 OD
22:28	0.28 OD
23:34	0.28 OD

Total Reduction in OD = 0.22 OD in 24 hr
Fig 4.0 – OD vs time for a 0.5 OD sample

The largest rate of change of optical density per time occurred during the post deposition or venting stage on the machine where a 0.16 OD (over a total measured reduction of 0.22) occurred over a 10-minute period. Within a one-hour period, a reduction in OD post machine of 0.19 OD was recorded. In 2 hours a 0.20 OD reduction was recorded, suggesting this would be a reasonable time in which to record more stable OD measurements from a metallizing cycle. For a 0.5 OD trial a reduction in OD of 44 % was recorded over a 24-hour period.
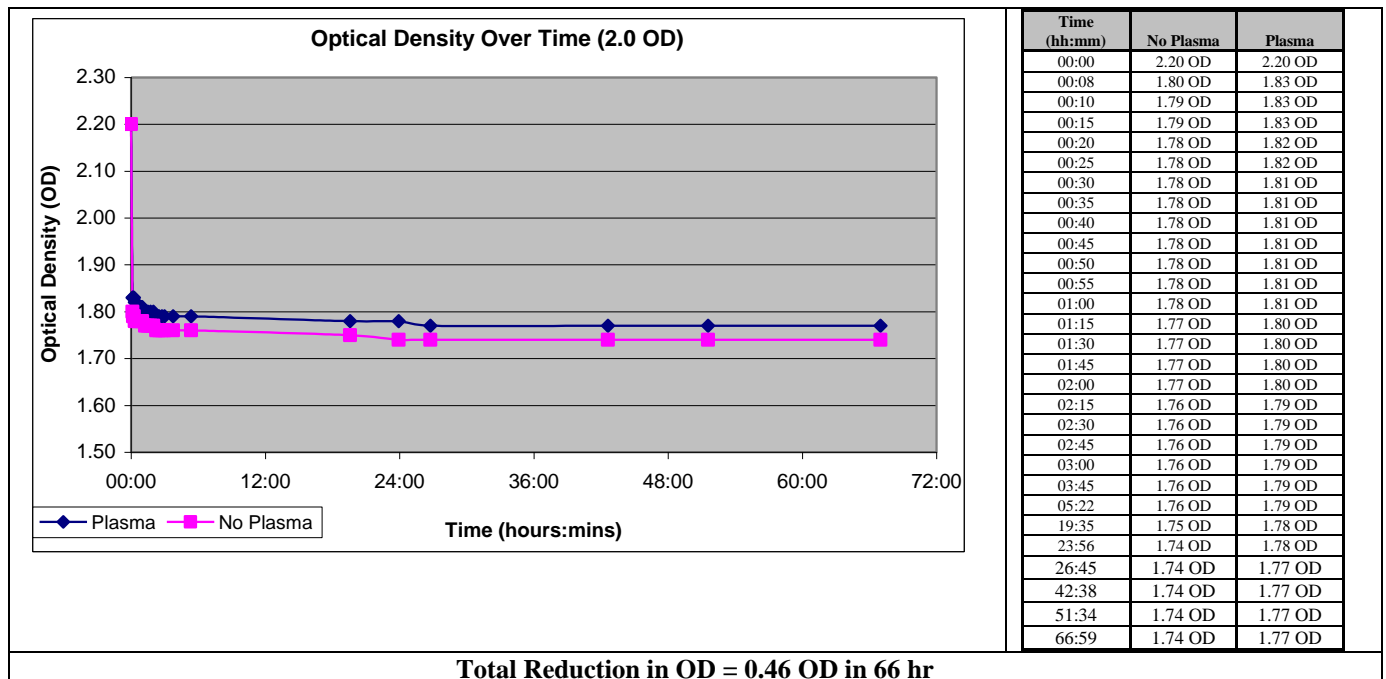
Figure chart: "Optical Density Over Time (2.0 OD)" with axes Optical Density (OD) from 1.50 to 2.30, Time (hours:mins) from 00:00 to 72:00. Legend: Plasma, No Plasma.

Time (hh:mm)	No Plasma	Plasma
00:00	2.20 OD	2.20 OD
00:08	1.80 OD	1.83 OD
00:10	1.79 OD	1.83 OD
00:15	1.79 OD	1.83 OD
00:20	1.78 OD	1.82 OD
00:25	1.78 OD	1.82 OD
00:30	1.78 OD	1.81 OD
00:35	1.78 OD	1.81 OD
00:40	1.78 OD	1.81 OD
00:45	1.78 OD	1.81 OD
00:50	1.78 OD	1.81 OD
00:55	1.78 OD	1.81 OD
01:00	1.78 OD	1.81 OD
01:15	1.77 OD	1.80 OD
01:30	1.77 OD	1.80 OD
01:45	1.77 OD	1.80 OD
02:00	1.77 OD	1.80 OD
02:15	1.76 OD	1.79 OD
02:30	1.76 OD	1.79 OD
02:45	1.76 OD	1.79 OD
03:00	1.76 OD	1.79 OD
03:45	1.76 OD	1.79 OD
05:22	1.76 OD	1.79 OD
19:35	1.75 OD	1.78 OD
23:56	1.74 OD	1.78 OD
26:45	1.74 OD	1.77 OD
42:38	1.74 OD	1.77 OD
51:34	1.74 OD	1.77 OD
66:59	1.74 OD	1.77 OD

Total Reduction in OD = 0.46 OD in 66 hr

Fig 5.0 – OD vs time for a 2.0 OD sample

For the 2.2 OD trial, the measurements were taken over a longer time period to determine the reduction in OD beyond the 24 hour period carried out for the 0.5 OD trial. Again, the largest rate of change of OD per time interval occurred during the post deposition or venting stage of the machine where a 0.4 OD (over a total measured reduction of 0.46) occurred over an 8 minute period. Within a one-hour period a reduction in OD post machine of 0.42 OD was recorded. In 2 hours a 0.43 OD reduction was recorded from an initial starting point of 2.2 OD. Beyond the 2 hr period, a reduction of 0.03 was recorded in the following 2 days. Again, this reconfirms that a minimum of 2 hours would be a reasonable time to start obtaining representative OD measurements, which had virtually reached an equilibrium condition. For a 2.2 OD trial a reduction in OD of 21 % was recorded over a 24 hour period.

Although the overall reduction in OD for the thicker aluminium layer was higher, although the relative reduction was lower for the thicker aluminium layer and reconfirms the hypothesis that the oxide layer formed protects the bulk aluminium layer from further oxidation. The oxide layer thickness measurements on the varying metal thickness trials determined via TEM measurements also illustrate this phenomenon (see Part II of the study).

The oxidation rates observed above are in agreement with the work conducted and presented by Mr. Glenn J Walters at SVC in 1990 [9], where he showed the following post metallizer oxidation pattern:-

Condition	OD
During Metallizing	0.55
After Metallization	0.35
48Hrs After	0.27
3 months after	0.21
Total degradation	**0.34**

Table 6.0 a table to illustrate the OD degradation over time from a previous study

The study shows the largest reduction on OD occurs between coating and venting the machine, although a larger percentage reduction of OD was found in the above study between a 48hrs to 3-month period.

OD versus thickness measurements

Optical density is a measure of the percentage light transmission through the film, and serves as a key measure of the light barrier properties of the product. However, the optical density for a given aluminium deposition is determined by the surface free energy of the polymer film surface. From this, it would be expected that the aluminium thickness vs.

optical density curve would be different for PET and orientated polypropylene or any other polymer film used for metallization. [10]

Sheet resistance measurements

Sheet resistance measurements were obtained offline using a GVE hand held resistance monitor and the following results were obtained:-

Statistical Analysis of Sheet Resistivity Results – 4 days aged

Statistical Analysis	Sheet Resistance (Ω/□)				
	0.5OD	1.0OD	1.5OD	2.0OD	2.5OD
Mean (Ω/□)	15.34	4.48	2.22	1.44	1.00
Standard Error	0.095	0.020	0.008	0.005	0.004
Median	15.38	4.48	2.23	1.43	1.00
Mode	15.83	4.50	2.23	1.47	1.00
Standard Deviation	0.573	0.117	0.047	0.030	0.023
Sample Variance	0.328	0.014	0.002	0.001	0.001
Kurtosis	-0.37	-0.80	0.26	-0.94	0.68
Skewness	-0.08	0.24	-0.39	0.03	-0.44
Range	2.40	0.47	0.20	0.10	0.10
Minimum	14.1	4.3	2.1	1.4	0.9
Maximum	16.5	4.7	2.3	1.5	1.0
Sum	552	161	80	52	36
Count	36	36	36	36	36
Confid. Level (95 %)	0.194	0.040	0.016	0.010	0.008

Table 7.0 – A table to illustrate the electrical performance obtained from the conducted coating trials

Statistical Analysis of Sheet Resistivity Results – 221 days aged

Statistical Analysis	Sheet Resistance (Ω/□)				
	0.5OD	1.0OD	1.5OD	2.0OD	2.5OD
Mean (Ω/□)	17.51	4.68	2.27	1.43	1.00
Standard Error	0.195	0.026	0.014	0.009	0.007
Median	17.60	4.70	2.30	1.40	1.00
Mode	17.90	4.80	2.20	1.40	1.00
Standard Deviation	1.172	0.157	0.085	0.053	0.045
Sample Variance	1.372	0.025	0.007	0.003	0.002
Kurtosis	2.39	0.02	-1.02	-0.78	2.64
Skewness	-1.11	-0.64	0.29	0.13	-0.14
Range	5.80	0.60	0.30	0.20	0.20
Minimum	13.5	4.3	2.1	1.3	0.9
Maximum	19.3	4.9	2.4	1.5	1.1
Sum	630	168	82	52	36
Count	36	36	36	36	36
Confid. Level (95 %)	0.396	0.053	0.029	0.018	0.015

Table 8.0 – A table to illustrate the electrical performance obtained from the aged conducted coating trials

In comparison with the OD changes over time, the sheet resistance measurements showed a much lower reduction in value over time and one explanation for this would be the fact that the device used to take the resistance measurements measures more of the bulk thin film resistance rather than the potentially oxidised surface of the aluminium. For the thinner aluminium layer of the 0.5 OD sample, the oxide layer affects more of the bulk material and a more significant change of resistance is observed.

GENERAL

Barrier measurements

Typical polymers used for packaging applications have permeation values for oxygen and water vapour that would either make them unsuitable for barrier packaging or require extremely thick films. Today thin film barrier layers such as metal and metal-oxides are used and provide much lower diffusion coefficients than the polymer materials. [11]

The thermal evaporation of aluminium from a ceramic evaporator onto polymer films is a standard technique that has been around for many years. Such films are widely used for food packaging, decorative, reflective and other technical applications. For food packaging, gas permeation is of great importance in order to maximise the products shelf life, and protection against light, oxygen and water vapour permeation is essential.

During the last fifteen years, the understanding of the metallized film barrier development has improved, and broad film barrier properties can be shown in terms of aroma, moisture and oxygen barrier for a wide range of metallized films.

Previous research has indicated little improvement in barrier performance once a critical thickness of aluminium has been achieved, but there is still a perception in the market that believe a thicker aluminium films will provide a higher barrier performance and the market is now asking for 3 to 4 OD on down gauged more heat sensitive substrates making more technical challenges for the metallizer manufacturer. The barrier properties of coated polymer film have been studied in several papers in which many different conclusions are reached. The various studies have agreed on the fact that barrier is controlled by the number and fractional area of pinholes, and increasing the thickness of the aluminium film does not dramatically change the number of pinhole defects and therefore the corresponding barrier level is not affected.

Research into barrier mechanism has been carried out by various groups and what have been concluded are the associated mechanisms for both water barrier and oxygen barrier are very different.

Oxygen permeation is dominated by macroscopic defects in the vacuum-coated barrier layers, which are largely caused by pin holes (areas of un-metallized material) potentially created from:-

- Physiochemical nature of the metal/polymer interface - Polarity issues with the surface of the polymer to be coated, where preferential film growth can cause uncoated or less coated regions on the film.
- Contamination on the polymer surface being metallized, which can become removed when unwinding.
- Ejection of aluminium in the form of 'spitting' from the ceramic evaporators.
- Interfacial roughness from anti-block additives, which vary in the form of physical size and density, can result in micron size protrusions breaking through the nm thickness coatings.
- Pinhole formation during crystallization.

For water vapour permeation, the mechanism appears less understood and conflicting theories have been put forward related to micro size defects via capillary action, degree of crystallinity and potentially permeation along grain boundaries.

Barrier measurements for this study were carried out as per ASTM 1249 and D3985 (unless stated otherwise) using a Mocon Permatran 3-33 for determining the water transmission rate through the metallized film and a Mocon Oxtran 2-20 for obtaining oxygen transmission rates. The results are illustrated below in table 9.0.

Post Machine/ Non-Aged Barrier Results

Oxygen Barrier = $cc/m^2/day$ (27 °C @ 50 % RH)
Water Barrier   = $g/m^2/day$ (37.8°C @ 90 % RH)

Description	Age (Days)	Oxygen Barrier ($cc/m^2/day$)/ (BIF)	Water Barrier ($g/m^2/day$)/ (BIF)
Base Material	0	140	40
0.5 OD Target Metal	25	2.80 (50)	14.38 (2.8)
1.0 OD Target Metal	19	1.98 (70.7)	1.76 (22.7)
1.5 OD Target Metal	19	1.78 (78.7)	1.64 (24.4)
2.0 OD	25	1.69 (82.8)	1.32 (30.3)

BOBST GROUP

Target Metal			
2.5 OD Target Metal	25	1.44 (97.2)	1.03 (38.8)
n = 2 for both OTR and WVTR assuming good barrier correlation was obtained			

Table 9.0 - A table to illustrate the barrier performance of the trials conducted
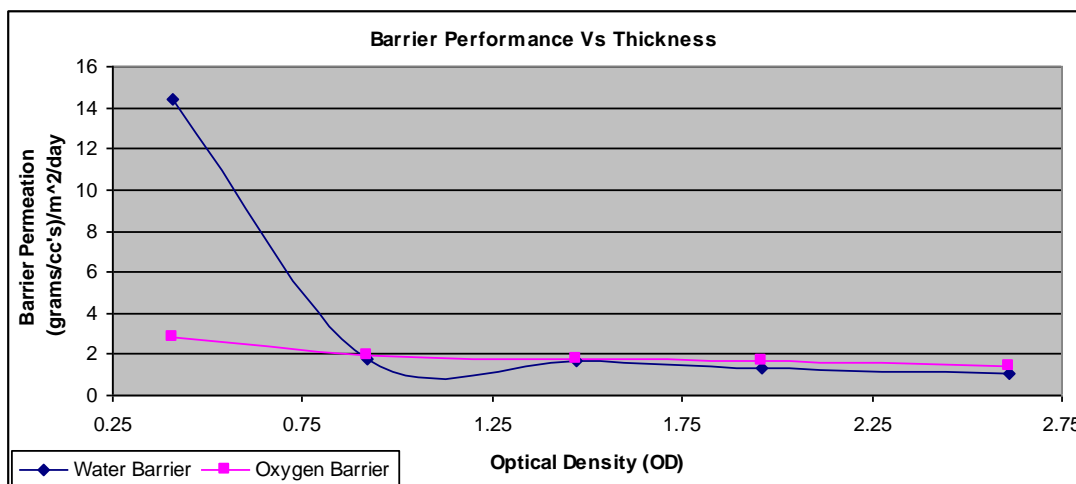

Fig 6.0 – A graph to show the relationship of barrier performance Vs optical density of the film

The data above clearly shows that a critical thickness for water barrier exists and a metal optical density of 1.0 corresponding to a metal total coating thickness of 11-17 nm is required to obtain a reasonable barrier improvement factor (BIF) from the base film. Below 11nm's or 1.0 OD, a sudden increase in permeation rate of water exists. For 1.00 to 2.50 OD an improvement in water barrier occurs with increase in metal thickness from a BIF of 22 at 1.0 OD to a factor of 39 at 2.5 OD. For oxygen barrier, we do not see such a dramatic increase in permeation rate with reducing metal thickness and a BIF of 50 is still achieved with a 0.5 OD or 11 nm coating. An improvement in oxygen barrier with thickness is observed from a BIF of 70 at 1.0 OD to 97 at 2.5 OD.

Based on the previously characterised changes in both optical and electricity properties of the thin film, barrier performance was investigated on 'aged' off machine samples where oxidation of the aluminium layer had occurred and the results are tabulated below:-

Aged Barrier Results

Oxygen Barrier = cc/m^2/day (***23•C*** @ 50 % RH)
Water Barrier = g/m^2/day (37.8°C @ 90 % RH)

Description	Age (Days)	Oxygen Barrier (cc/m^2/day)/ (BIF)	Water Barrier (g/m^2/day)/ (BIF)	Off Machine Optical Density
0.5 OD Target Metal	183	2.13 (65.7)	11.15 (3.6)	0.38 OD
1.0 OD Target Metal	182	1.43 (97.9)	1.96 (20.4)	0.90 OD
1.5 OD Target Metal	181	1.16 (120.7)	1.34 (29.9)	1.43 OD
2.0 OD Target Metal	180	1.02 (137.3)	1.78 (22.5)	1.94 OD
2.5 OD Target Metal	177	0.82 (170.7)	1.33 (30.1)	2.49 OD
n = 2 for both OTR and WVTR assuming good barrier correlation was obtained				

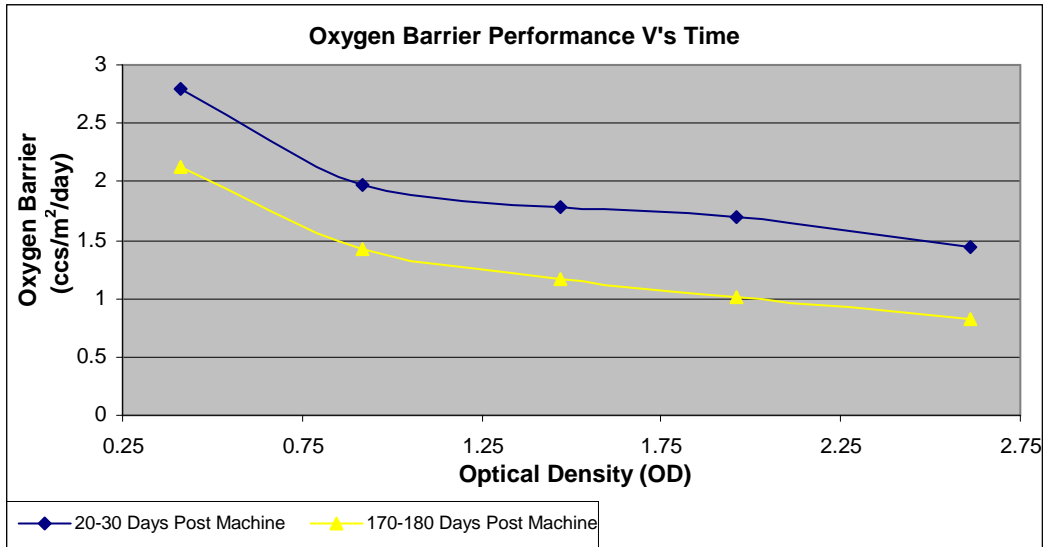**Table 10.0 - A table to illustrate the barrier performance of the aged trials conducted**

Fig 7.0 – A graph to illustrate oxygen barrier performance vs optical density on two aged samples

Although a general improvement in oxygen barrier of 20-40 % was observed with the aged samples, the reduction in measuring temperature is responsible for the reduction in permeation rates where it has been reported that permeation rates typically change 5-7 % per °C in testing temperature. [13]
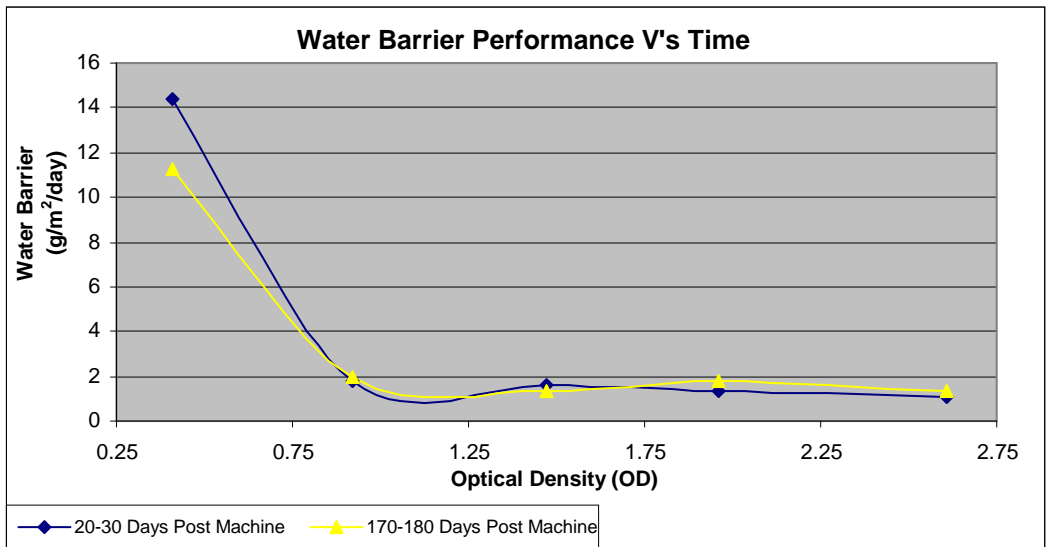

Fig 8.0 – A graph to illustrate water barrier performance v's optical density on two aged samples

An improvement in water barrier with time is observed for the lowest, 0.5 OD sample following 180 days of aging in a laboratory subjected to an ambient condition of 19-20 °C and 50-60 % RH. For thicker or higher OD samples, no significant change is observed and any smaller scale changes in permeation rate measurements can be attributed more to the normal variance in barrier level measurements when testing metallized films.

It has already been established that the most significant change in the aluminium film properties occurs during the first 48 hours from the metallizer. Based on this phenomenon the short-term barrier effects due to oxidation were investigated with samples taken immediately off the metallizer. The barrier performance and results of these short-term oxidation trials are tabulated below in Table 10.0.

The base substrate for the additional short term oxidation trials was 12 micron corona treated polyethylene terephthalate but from a different manufacturer, and therefore reference back to the longer duration oxidation trials cannot be made. Based on this, the base barrier performance of this substrate was made and all stated BIF factors are relative to the base film.

Barrier Properties – Effect of Aging – Fresh Metal Samples

Description	Age	OTR (cc/m^2/day)/ (BIF)	WVTR (g/m^2/day)/ (BIF)
Base Film	-	138	38
0.5 OD Metal	0*	1.99 (69.3)	16.37 (2.3)
0.5 OD Metal	10	3.4 (40.6))	15.64 (2.6)
2.0 OD Metal	0	0.44 (313.6))	0.72 (52.8))
2.0 OD Metal	10	0.47 (293.6)	0.50 (76)
n = 2 for both OTR and WVTR assuming good barrier correlation is obtained			

Table 11.0 - A table to illustrate the effect of oxidation on barrier performance

From the results tabulated in table 11.0 it appears the oxygen barrier is detrimentally affected to exposure to air when a thinner aluminium layer is used, although more barrier measurements would need to be conducted to determine the validity of this conclusion. The same effect does not exist for the thicker 2.0 OD metal sample where short-term oxidation does not appear to affect the oxygen permeation rate of the film.

For water permeation, oxidation of the aluminium layer appears to improve the performance of the film and this appears more apparent on the thicker 2.0 OD sample.

Barrier changes on the Mocon barrier testing equipment
Based on the changes in barrier performance post machine, a further study was carried out to monitor the effects over time of the metallized film subjected to the testing conditions of the Mocon equipment where elevated temperatures and humidity existed for the Permatran unit, which measures WVTR, and a slightly higher temperature existed for the Oxtran unit, which measures OTR. The 0.5 OD sample was selected for the trial as this had been found to exhibit the largest BIF change.

Prior to conducting the characterisation work on the Mocon equipment, the time to reach equilibrium for an oxidised sample was established and found to be 1 to 2 hours.

Oxygen barrier
During the conditioning phase of the test cycle, several measurements were taken to try and characterise the performance of the film when subjected to the set test conditions with the intention that the barrier performance of the aluminium film subjected to varying degrees of oxidation could be determined. Does aluminium oxide provide a better barrier per thickness performance than less reacted aluminium?

The two graphs below in Fig 9.0 and 10.0 illustrate the magnitude and profile over time of the oxygen and water permeation rate of a fresh sample installed into the Oxtran/ Permatran units immediately after venting the machine and one that had been stored in the laboratory for a period of 10 days.
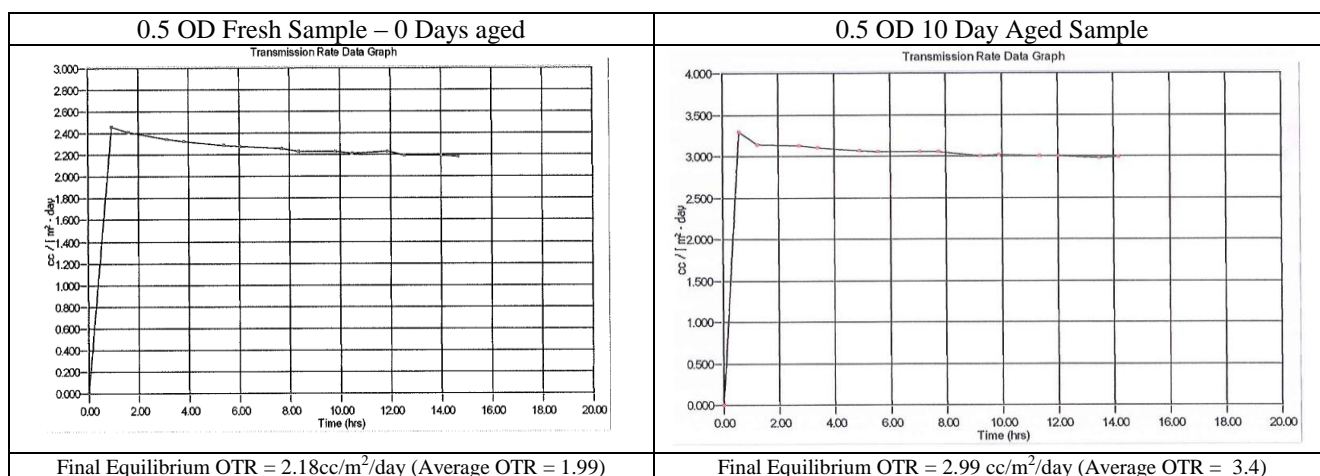
0.5 OD Fresh Sample – 0 Days aged	0.5 OD 10 Day Aged Sample
Final Equilibrium OTR = 2.18cc/m^2/day (Average OTR = 1.99)	Final Equilibrium OTR = 2.99 cc/m^2/day (Average OTR = 3.4)

Fig 9.0 – A graph to illustrate oxygen performance over time on the barrier testing equipment

For oxygen barrier, the general shape representing the oxygen permeation rate over time was consistent with the fresh and aged samples for all four trials conducted, but the actual magnitude of the permeation rate for aged sample was

significantly higher than the fresh sample straight from the metallizer. A possible explanation for this is the aged sample is more oxidised and this coating stoichiometry provides a better mechanism to allow oxygen permeation.

Water Barrier
For water barrier, the magnitude of the permeation rate was found to be similar once an equilibrium condition is achieved. However, the profile shape representing the permeation rate over time are quite dissimilar, and suggest the coatings take a different time interval to reach an equilibrium permeation condition, or, the different thin films genuinely have different performances to water permeation and a less oxidised aluminium layer provides a better barrier against water ingress.
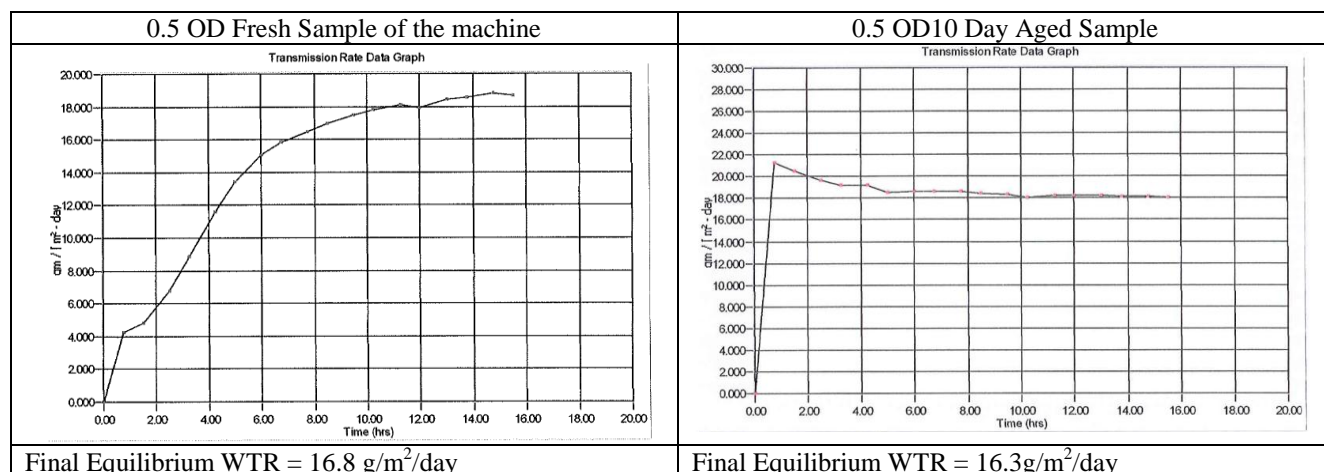
0.5 OD Fresh Sample of the machine	0.5 OD10 Day Aged Sample
Final Equilibrium WTR = 16.8 g/m^2/day	Final Equilibrium WTR = 16.3g/m^2/day

Fig 10.0 – A graph to illustrate water performance over time on the barrier testing equipment

On hypothesis to explain this is that on a fresh aluminium sample, there is still a high level of un-reacted fresh aluminium near the surface, the MVTR appears to offer an improved barrier reading as during the adsorption phase it is likely that water dissociates into hydrogen and oxygen before diffusing through the bulk material and desorbing from the opposite side. With a fresh coating, the oxygen reacts with "virgin" aluminium during adsorption therefore providing less oxygen to recombine with the hydrogen, therefore providing lower MVTR results initially.

On an aged sample, the amount of free aluminium is less at the surface, resulting in less reaction of oxygen and more recombination of hydrogen and oxygen giving quicker equilibrium with similar final results**.** The surface energy of the top surface and the ability of water to adsorb initially also changes depending on age and this also affects the equilibrium time.

A SIMS study carried out in a previous study has shown that there is a chemical interaction between the diffusing water vapour and barrier layer, which promotes dissociation of the H_2O, and that this interaction is significant in controlling the activation energy for permeation

Summary/ Conclusions
We have measured the optical, electrical, and barrier properties of aluminium films with their oxide layers as a function of aluminium film thickness and time. We have also measured the variation in the optical density as a function of down web and cross web position on the substrate. The films were produced in thicknesses corresponding to optical densities of approximately 0.5 to 2.5 in 0.5 OD steps which corresponds to physical thicknesses of about 6-40 nm. A summary of the results obtained is given in table 12.0 below.

Average	Uncoated	0.5OD	1.0OD	1.5OD	2.0OD	2.5OD
Optical Density (OD)	0.040	0.409	0.922	1.470	1.950	2.578
Sheet Resistance (Ω/□)	n/a	15.338	4.475	2.224	1.441	0.997
Water Barrier (g/m²/day)	~40	14.38	1.76	1.64	1.32	1.03
Oxygen Barrier (cc/m²/day)	~140	2.8	1.98	1.78	1.69	1.44
Total Coating Thickness (nm)	0	11.8	18.8	25.2	34.7	43.3

Table 12.0 - A summary table to illustrate the optical, electrical and physical properties of the trials performed

The study has highlighted the significant changes in optical density levels that exist over time from point of deposition of the metal in the vacuum metallizer, through to the time when the metallized sample may be measured. It has hopefully helped to illustrate the practical importance for the producer or converter of aluminium metallized film to quote a time post deposition when the OD levels were measured, to enable accurate quantitative comparisons to be carried out. In addition to the optical changes with time, the electrical properties of the film are also affected via oxidation of the reactive aluminium layer but these have been found to be of a lesser degree, possibly due to the measurement of the less reacted bulk of the material, and not the partially oxidised surface material.

The work on barrier measurements has illustrated the typical barrier improvement factors that are achievable on varying metal thicknesses from 6 nm through to 37 nm. The study has also illustrated that increasing the metal thickness beyond a critical thickness of approximately 12 nm does not necessarily provide the same level of barrier enhancement that some in the industry assume may be the case. A 30 % improvement in barrier would require up to 300 % more metal deposition.

The previous data, widely used in the industry illustrating metal thickness as a function of optical density has provided a useful tool for many years, although there was some concern over the accuracy or validity of the published data. With the aid of newer more accurate preparation and measurement techniques, the authors have produced a different set of metal and oxide thickness values for a given metal optical density level and different techniques have shown the associated coating thicknesses to be considerably higher than those previously published. These are covered in part II of the study.

Based on the current market trends of vacuum metallization where the industry is requesting higher deposition levels and higher associated optical densities, the authors would recommend further investigations extending the optical density level from 2.5 to 4.0 OD. An extension to the study should also include plasma pre treatment with particular focus on the barrier performance of the metallized film and metal bond strength using some of the more commonly used gas and power recipes.

Acknowledgments

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7 Barrier Properties of Metallized Films – Bernard Henry – Aimcal Technical Reference, 4th Edition, July 2007. Page 35

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