R2R pilot line production of high performance moisture barrier films

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1. Introduction

Holst Centre started in 2006 with the development of technologies for transparent flexible ultra-moisture barrier encapsulation of OLEDs and OPVs utilizing sheet-to-sheet (S2S) processing approach. Our partners successfully commercialized Holst Centre S2S encapsulation technology, but to further reduce cost and to make a major step towards mass produced ultra- moisture barrier, in 2012 Holst Centre set up an unique roll-to-roll pilot line with capability to deposit multilayer barrier coatings on foil. This tool combines PECVD deposition of inorganic coatings with a possibility to slot-die coat organics. These R2R barrier films are used within Holst Centre and by several partner companies of Holst Centre. This paper will discuss the latest R2R multilayer barrier development, performance and the end results from R2R encapsulated OLEDs.

2. R2R barrier film pilot line (Rollcoat)

2.1 R2R pilot line overview

Photo 1: R2R barrier film pilot line

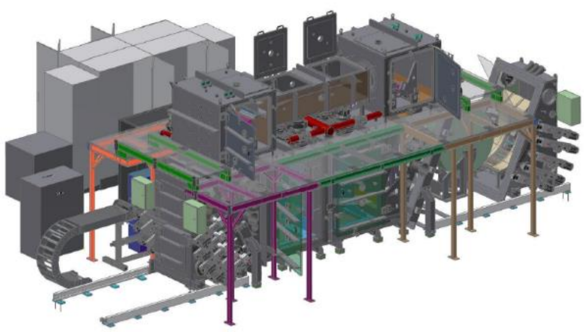


Figure 1: 3D drawing of R2R barrier film pilot line

In 2012 the unique R2R pilot line (Rollcoat) was installed to develop R2R thin film transparent flexible and low cost barrier films on 40 cm wide and 500mtr length foils that can be used for OPV and OLED applications. At the start only a low grade moisture barrier could be produced which consist of a PET foil in combination with a single layer of PECVD silicon nitride, typical WVTR values in the range of 10^{-4} g/m2.day @20°/50%RH with a pinhole density of >20ph/cm^2. In 2014 after the introduction of a slot die coating system it was possible to coat a planarization layer on the PET foil with subsequent deposition of PECVD silicon nitride. This was a major step towards high grade moisture barrier quality. In combination with process and equipment optimization, particle reduction, liner film lamination, regular maintenance checks and process control it was possible to produce reproducible high grade moisture barrier films with a WVTR of <5.10^{-6} g/m2.day @20°/50%RH with a low pinhole density of 0.05-0.5ph/cm2 for a 20µm planarization layer with a

200nm thick SiN layer. This barrier is ideal for flexible OPV applications but due to the pinhole amount still not good enough for OLED devices. For non-emissive OPV devices some pinholes are not a problem (a few percent reduction of the functional area of an OPV cell during the lifetime is acceptable). For emissive OLED devices this is far more critical: one black spot of 100µm is a failure (for a 10x10cm OLED device a 1ppm reduction of the functional area is already a failure!!). In 2016 the R2R development of a high performance moisture multilayer barrier for OLED applications started. See section R2R multilayer barrier development for further information.

2.2 Barrier deposition in the Rollcoat

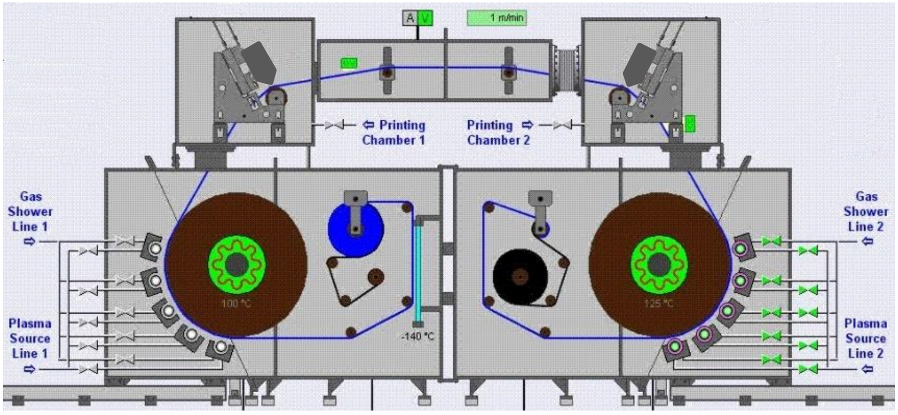


Figure 2: Barrier deposition in the Rollcoat

The R2R barrier pilot line is developed for plasma based deposition processes and organic coatings. The system is completely under vacuum and consists of loading, unloading, plasma and printing/coating chambers with a web handling and protective liner lamination system. The processing side of the foil is never touched by any rollers (only touching on the backside of the foil). The maximum foil width is 400mm and length 500mtr with typical deposition speed of 0.5 - 2 m/min. R2R deposition options are: silicon nitride, silicon oxide (high rate low temperature deposition) and oxygen plasma. Coating options are: R2R planarization coating, getter coating and topcoat. The ambition for the R2R line is to develop a thin film transparent flexible and low cost barrier film on a flexible substrate that can be used for OPV and OLED applications.

3. R2R barrier quality measurements

The quality of the barrier film is measured by the amount of water which is going through the barrier film per unit area, per unit time. This is expressed as the water vapor transmission rate (unit: $g/m^2/day$). For a single barrier layer the overall WVTR is equal to the intrinsic WVTR (WVTR-i) + Extrinsic WVTR (WVTR-e). The intrinsic WVTR depends on the porosity and thickness of the barrier. The extrinsic WVTR depends on the number of pinholes in the layer, this is caused by particles, roughness and external damage. For a good barrier layer the extrinsic WVTR is dominant.

The WVTR-i is determent by accelerated calcium tests at 60°C/90%RH conditions: Ca reacts with water and becomes transparent which is used to determine the WVTR of the tested film. The extrinsic WVTR-e is determined by a new developed large area pinhole density test: a special moisture sensitive adhesive is used to bond two barrier films against each other. This adhesive is a non-transparent milky coating which becomes locally transparent at places where the moisture permeates the barrier film (photo 2). The number of saturated spots in the adhesive is counted with image processing software typically after 10 days at 85°C/85%RH and the WVTR-e is determined.

The acceleration factors are: 20x for 60°C/90%RH conditions, 60x for 85°C/85%RH conditions compared to 20°C/50%RH conditions.

This moisture sensitive adhesive is an acrylic UV curable adhesive with 5% CaO added. The advantage compared to a Ca test is that it can be easily applied by inkjet printing on a large area and the acceleration test can be done at 85°C/85%RH. Disadvantages of the Ca test are: long test time needed, Ca deposition is done in special vacuum equipment (sizes are limited), max temp/relative humidity conditions are 60°C/90%RH due to gas/bubble formation by H2 release at higher temperatures.

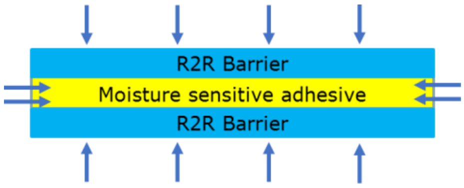


Figure 3: For the pinhole density test two barrier foils are laminated against each other with a special moisture sensitive adhesive in between.

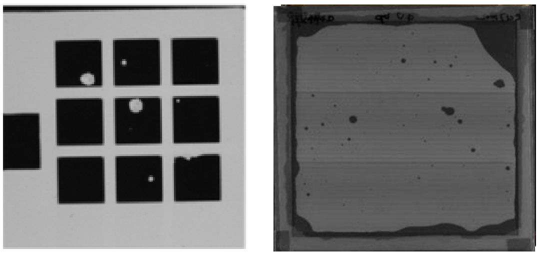


Photo 2: Photo of a Ca test for 9 pads each with an area of 2.25 cm^2 (left) and a large area 12 cm x 12 cm pinhole density test (right) sample

4. Results R2R multilayer barrier development

4.1 Multilayer stack development with organic getter coatings

The multilayer barrier which has been developed for R2R OLED applications consists of an organic coating for planarization (OCP) and two inorganic barrier layers of silicon nitride with a special organic getter coating (OCPg) in-between. Because the top SiN layer can be easily damaged when R2R rewinding is done on a roll, a protective liner film is laminated on top. The effect of this multilayer stack is decoupling of pinholes in the two SiN barrier layers and diffusion delay of water by the introduction of a relatively thick getter layer.

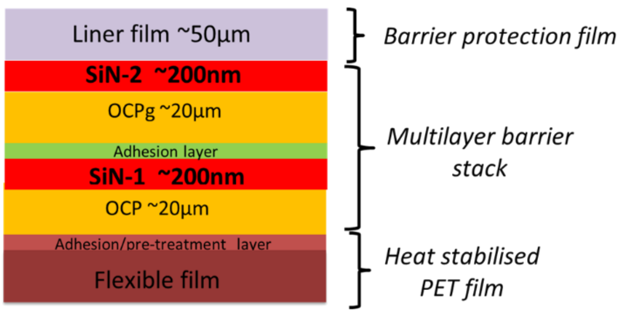


Figure 4: R2R multilayer stack on PET film

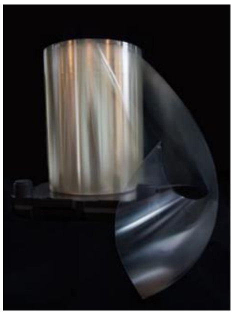


Photo 3: Barrier film roll.
Width 400mm, length 500mtr

The organic getter coating is specially developed together with our coating supplier Rolic Technologies for slot die coating in a vacuum system. The coating contains nanoparticles of water absorbing material in the organic layer and the lateral water transport is delayed. There are different water absorbing materials available with different concentrations. Together with our coating supplier two potential materials are tested for R2R applications: nano CaO and nano Zeolite particles dissolved in an organic coating. The organic coating is a UV-curable acrylate with no solvents.

Important is to have a good adhesion of the layers. Here two problems occur. First the adhesion of the organic coating on a plain PET surface is very weak. This is solved by introducing an extra adhesion/pre-treatment layer on the PET by our foil supplier DTF. A more challenging adhesion problem is the adhesion of an organic coating on an inert SiN surface. This problem has been solved by introducing an extra gas to the system (N_2O) which makes it possible in combination with SiH_4 to deposit a very thin SiO_x PECVD layer on top of the SiN layer. This very thin SiO_x adhesion layer improves the adhesion (cross cut tests show adhesion of 30 to 100% depending on which coating material is used).

4.2 Optical quality R2R multilayer barrier

Optical UV-VIS measurements show that there is no light absorption in the visible spectrum range for the multilayer as single layer barrier.

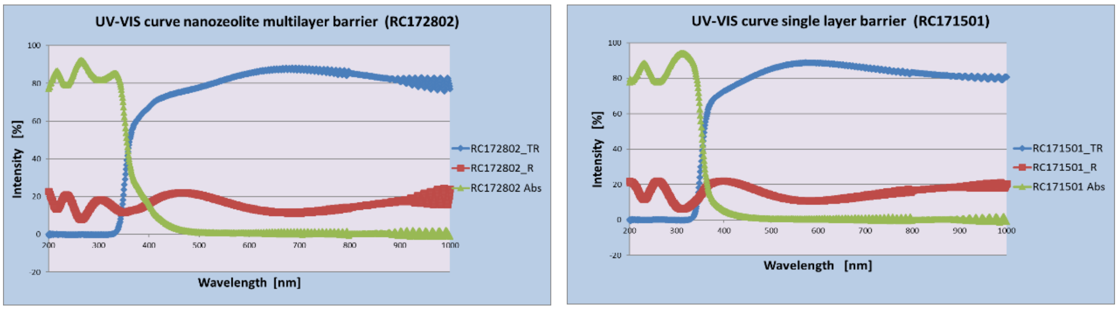
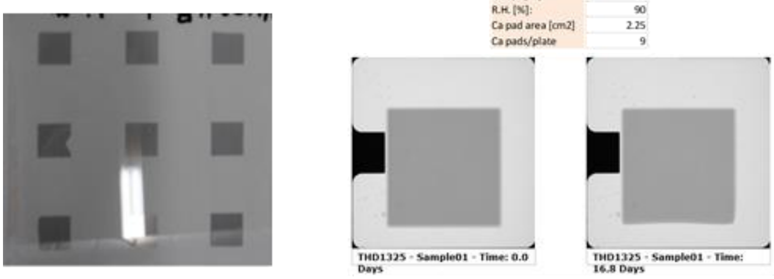


Figure 5: UV-VIS curve for nanozeolite multilayer and single layer barrier film.
Avg. transmission (360-780nm) multilayer barrier: 80.1%, single layer barrier 83,1%.

4.3 R2R Multilayer WVTR measurements and pinhole tests

Typical intrinsic WVTR values for a single layer barrier (only one SiN layer) measured with the optical Ca test are ≤ 5.10-6 g/m2/day@20°C/50%RH. Also MOCON Aquatran-1 tests done on this single layer barrier show very good WVTR values, these are below the detection limit (<5.10-4 g/m2/day@38°C/90%RH). But as mentioned before this is still not good enough for OLED, due to the amount of pinholes (~0.05-0.5ph/cm2).



Temp. [°C]:	60
R.H. [%]:	90
Ca pad area [cm2]	2.25
Ca pads/plate	9

WVTR 60/90RH [g/m²/day]		Amount pinholes
average	std	/cm2
4.1E-05	4.5E-06	0.03
1.7E-05	6.7E-06	0.03
1.5E-05	6.7E-06	0.05

WVTR 20°C/50%RH ≤ 2.10-6 gr/m2/day !!

Photo 4: Example of an optical Ca test for WVTRi measurements

The new multilayer barrier shows a huge reduction in amount of pinholes. This is clearly visible with the WVTRe/pinhole count test. A first R2R batch with multilayer barrier with nanozeolite getter (PET-planarization-SiN1-nanozeolite getter coating-SiN2) shows 0 saturation spots after 139days 85°C/85%RH. This corresponds with 0 spots in 20 years at 20°C/50%RH. However the base material (single barrier layer) was also of very high quality. A second batch shows the difference more clearly.

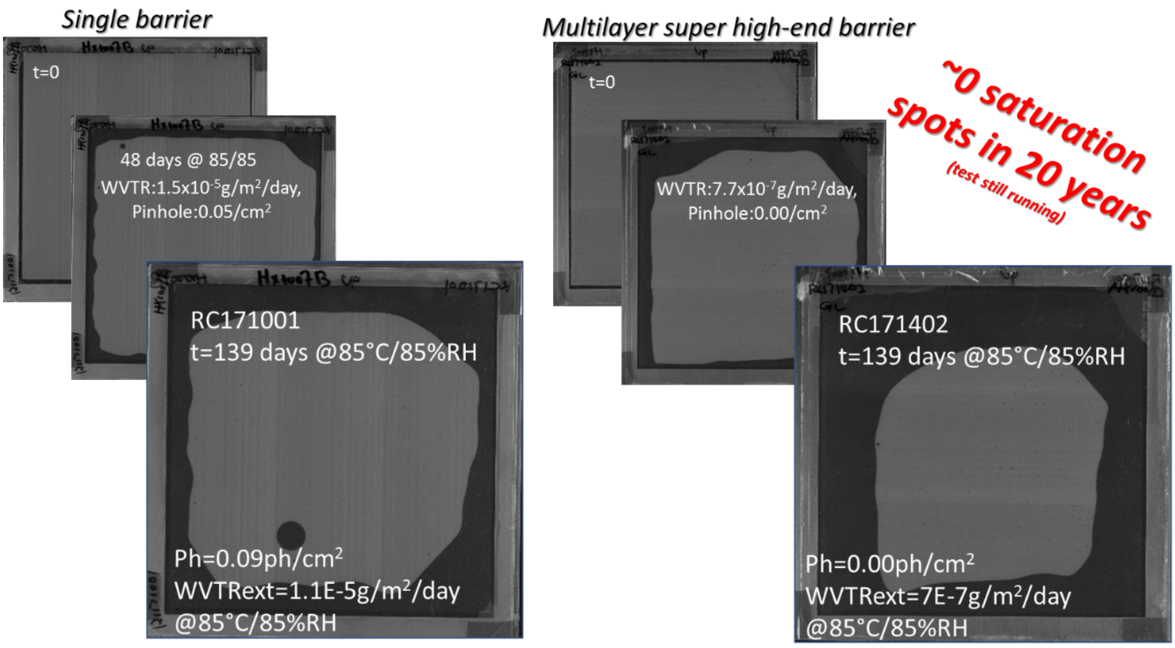


Photo 5: WVTRe/ pinhole test on single and nanozeolite multilayer barrier

2nd Batch with multilayer barrier with nanozeolite getter and improved adhesion (PET-planarization-SiN1-adhesion layer-nanozeolite getter coating-SiN2):

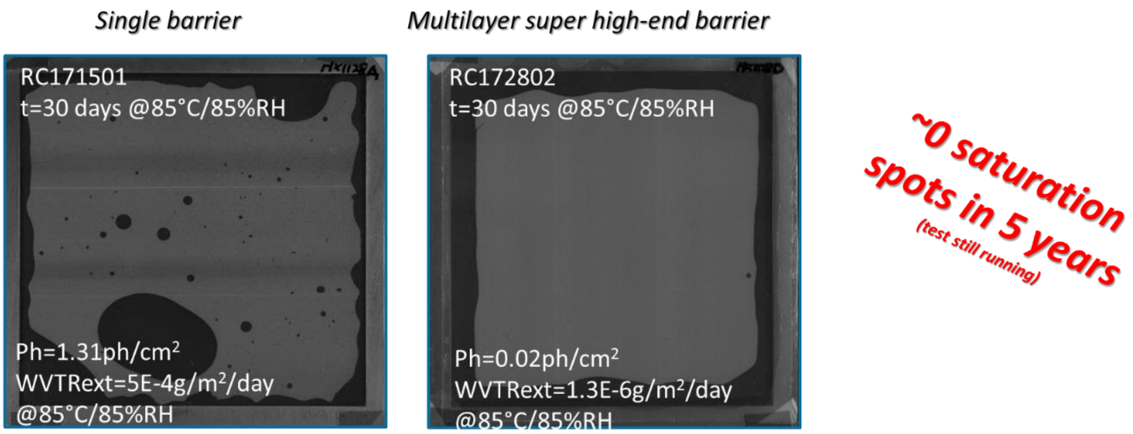


Photo 6: WVTRe/Pinhole test on second batch of single and nanozeolite multilayer barrier with improved adhesion

A 3th batch with multilayer barrier and nano CaO getter (PET-planarization-SiN1-CaO getter coating-SiN2) shows also huge improvements:

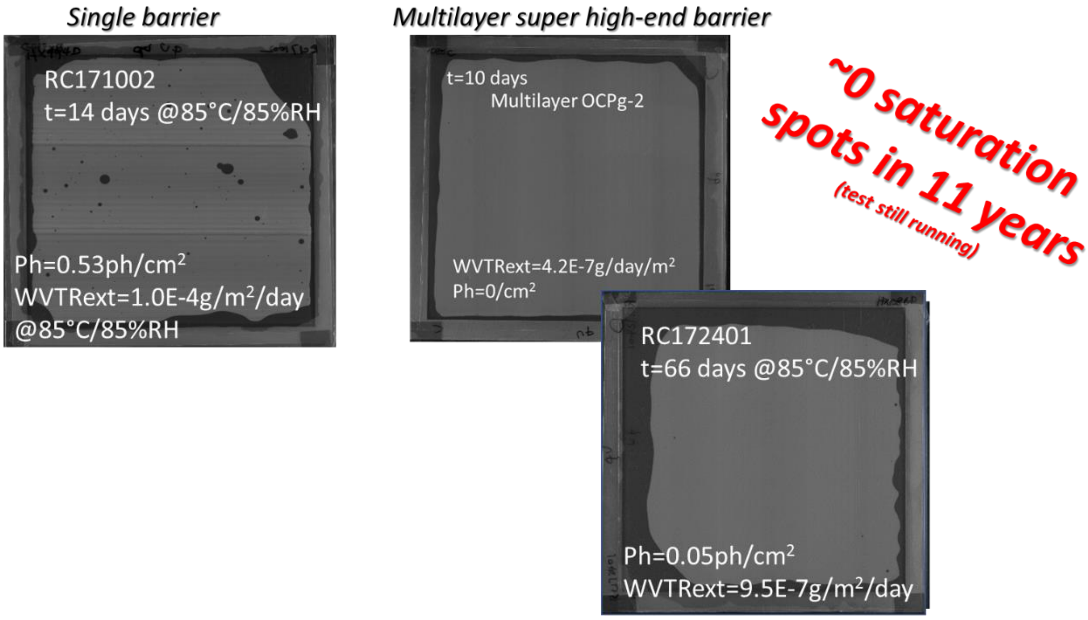


Photo 7: WVTRe/pinhole test for single and OCPg 0.15% CaO multilayer barrier

4.4 Side leakage of barrier film

The current planarization layer in the Rollcoat is applied with a slot die coater and the inorganic SiN layer is enclosing this organic coating. Due to this enclosure no side leakage will occur into the organic layer. But when the barrier is cut to device dimensions side leakage will occur into the organic layer. This side leakage effect has been measured in our S2S line by depositing a thin layer of Ca on a glass plate (fig.6) . The water ingress through the coating/adhesive can be monitored by the decrease of the Ca pad [1]. The Ca is converted into $Ca(OH)_2$ and gets locally transparent. With the aid of a high resolution camera and image processing software the side leakage rate can be measured (fig. 7).

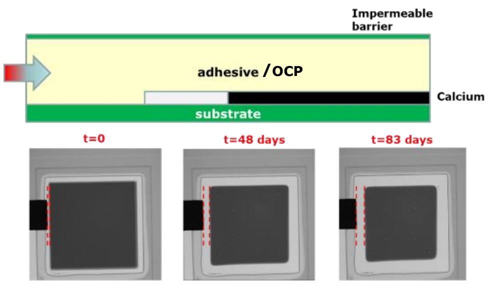


Figure 6: Side leakage measurements at 60°C/90%RH

material	side leakage	spot growth	
	[mm/hrs$^{0.5}$]	[mm^2/hrs]	rel to 5% CaO
plain OCP	0.75	0.56	10.6
OCP 0.15% CaO	0.60	0.36	6.8
OCP 5% CaO	0.23	0.05	1.0
nano-zeolite	0.40	0.16	3.0

Figure 7: Side leakage rate and spot growth at 60°C/90%RH

The best performance is for OCP with 5% CaO. But the disadvantage of this 5% concentration is the milky appearance (not transparent) that creates dark spots when water penetrates through pinholes and cause local saturation. Most promising OCP for OLED barriers is the nano-zeolite or 0.15% CaO getter, which are completely transparent (fig. 7).The performance of nano-zeolite is between 0.15% and 5% CaO getter OCP. The spot growth numbers reflect the first step in black spot formation when

SiN-OCP-SiN is applied on an OLED ("time-to-overlap"). If the next step (growth of black spot when water reaches the pinhole in the cathode) behaves similar, the last column in the table reflects also the relative shelf lifetimes. Indeed, we found an order of magnitude difference in shelf lifetime between plain OCP and 5% CaO getter OCP[2].

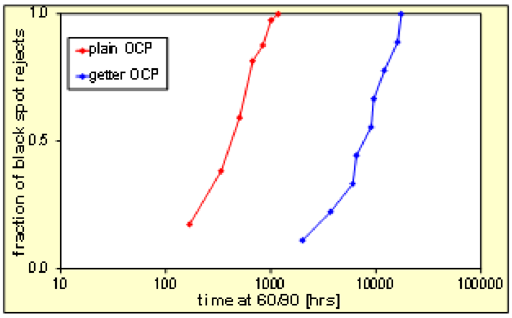


Figure 8: Fraction of black spot rejects in S2S OLED device. For plain OCP and getter OCP (5% CaO)

5. Conclusion

The barrier pre-pilot line (Rollcoat) is capable of producing high quality single layer barrier films on 40cm width heat stabilized PET films with an intrinsic WVTR of <5.10-6g/m2/day and a pinhole density of ≤0.5 ph/cm2. This barrier quality is perfectly suited for all kind of flexible OPV applications. Recently for a flexible OPV customer 1200m2 of this foil has been produced. Although WVTR values are very good, if used for OLED devices this barrier would still result in detectable black spots due to the (low) number of pinholes.

The recent development of a R2R multilayer barrier which contains a special organic coating with nano getter particles shows a huge reduction of the amount of pinholes. On this moment still the evaluation is going on for the most suited organic getter coating, which is located between the two inorganic SiN barrier layers. This relative thick getter coating decouples the pinholes in the very thin SiN barrier layers and delays the progress of water ingress in the layer by a factor of ~10. This leads to a multilayer getter barrier which is suited for OLED applications. Process optimization and R2R OLED testing is already going on and will be reported beginning of 2018.

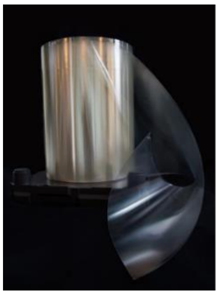


Photo 8: Photo of a barrier reel 400mm width and 500mtr

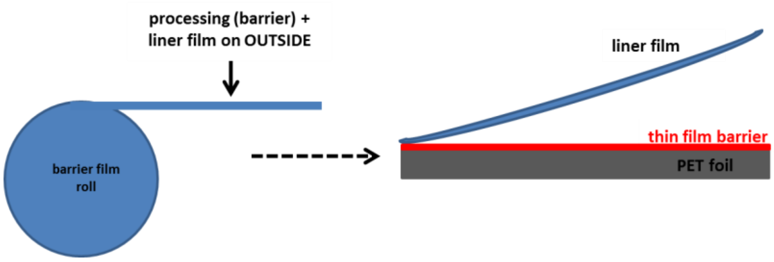


Figure 10: Drawing and cross section view of a barrier reel.

References:

1. J.J. Michels *et al.*
   A combined experimental and theoretical study on the side ingress of water into barrier adhesives for organic electronics applications
   Journal of Materials Chemistry, C **2**, 5759 (2014)

2. P. van de Weijer, P. Bouten, S. Unnikrishnan, H. Akkerman, J. Michels, T. van Mol
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