Polymer web surface cleanliness.

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ABSTRACT

The volume of polymer films produced each year increases as vacuum coated film sales increase and more applications are found for its use. A number of the newer applications such as optical data storage, organic light emitting devices, all polymer displays, anti-reflection coatings and barrier films require the surface of the polymer web to be smooth, flat and clean. In many of the new applications the films have had to have some increase in performance. Many of these film attributes, such as improved tensile performance, lower shrinkage or higher clarity, can be easily specified. However the surface quality, whilst it is becoming a more critical factor in many applications, is often allowed an undemanding specification when purchased. It is common for little or no mention of it to be included in the specification and the responsibility for achieving the required level of cleanliness to fall on the user rather the manufacturer. In this paper I will show where much of the contamination meets the film surface and what may be done to improve the film surface quality both during manufacture and afterwards.

INTRODUCTION

Polymer webs do not have perfect surfaces onto which vacuum thin film coatings are deposited but for many applications this does not matter. The surfaces may have an inherent surface roughness and in addition will have some defects introduced by the entrapped debris wound into the rolls. The debris type and size can vary hugely depending upon the manufacturing process, the manufacturing site and even the season of manufacture. There are an increasing number of applications where the level of contamination directly limits the performance of the devices. The thickness of many of the vacuum deposited coatings is often very much thinner than the contamination that is present on the surface. Typically thin single layer transparent barrier coatings are of the order 20nm whereas some of the debris could be expected to be several microns in diameter.

Optical Data Storage (ODS) systems based on a laser of 830nm where the laser is focused down to 0.8 microns diameter have tracks written 1.4 microns apart. To achieve a product with the required overall bit error rate of 1 x 10^{12} means the vacuum deposited coating needs to have no more than 1 defect of >0.3 microns in a 0.8mm square. As the laser wavelength is reduced the spot size is reduced as is the track spacing and this gives an increase in the storage density. The bit error rate has, at worst, to stay the same and this requires the numbers and size of the defects to be reduced. In this application, as well as the surface debris, dimples in the surface, from debris pressed into the surface but then removed, cause scattering of the read laser and hence errors.

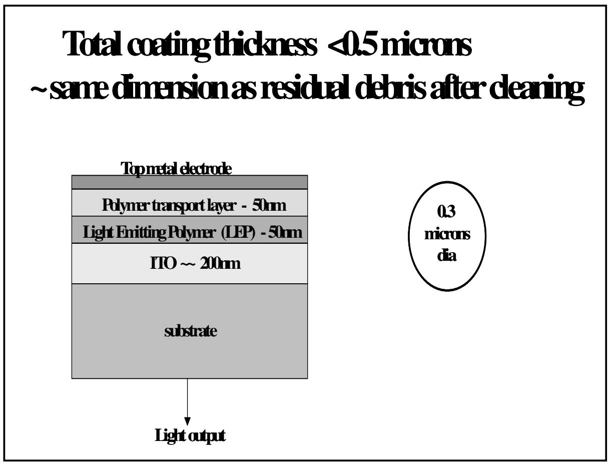

Figure 1. The structure of an Organic Light Emitting Display (OLED) highlighting the total coating thickness compared to debris size.

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In Organic Light Emitting Displays (OLEDs) the polymer light emitting layer and the polymer transport layer are both only 50nm thick as shown above. Thus any defect on the surface that is proud of the surface by 100nm or more is likely to be of concern. The OLEDs are sensitive to contamination and require a barrier coating. The level of barrier required to give the desired operational lifetime is orders of magnitude better than the barrier coatings that are generally used for food barrier applications.

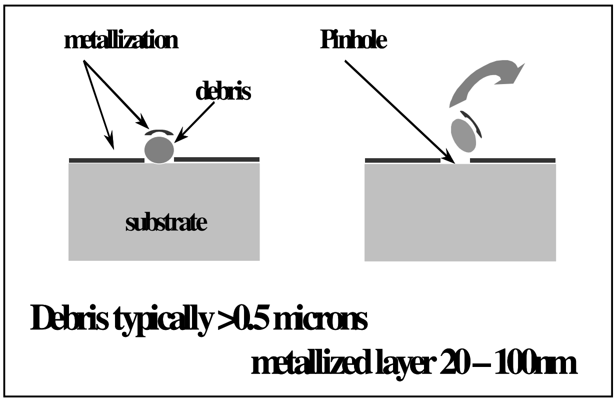

Figure 2. The formation of pinholes by the removal of debris after vacuum coating.

In barrier applications it has been shown the barrier performance of either the metal or oxide vacuum deposited coatings to be limited by the number of pinholes present in the coating. Work was done to show that the pinholes were primarily caused by debris on the surface of the web being moved following vacuum coating leaving holes in the coating as shown in Figure 1. (Refs 1 & 2)

COUNTING DEFECTS

The first step in counting defects is to define what constitutes a defect. Webs used in barrier applications may only need to include the debris sitting on the surface, that will result in a pinhole, in the definition of a defect. Webs used for ODS applications where other surface defects such as bumps or dents in the surface can be a problem need to have them included. In this study bumps, dents and debris were all included in the count of defects.

As the polymer web is transparent and defects small, typically below the limits of optical resolution of the eye, they are difficult to see without magnification of some type.

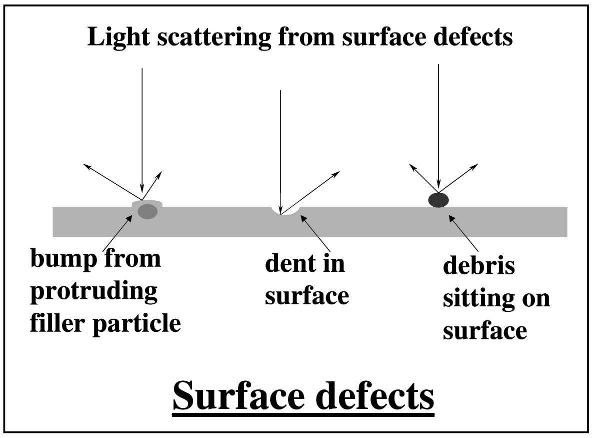

Figure 3. A schematic of the different types of defect detected in the web surface.

In looking for fine defects I am personally suspicious of contact techniques using a stylus to produce a surface profile. I remain to be convinced that debris on the surface is adequately included in the surface profile produced. The stylus will just push through the debris and only record the polymer profile. Typical results are described in Ref. 3 where the authors resolve the polymer chains but do not refer to any surface debris. The likes of the tapping mode atomic force microscopy could be used but it takes a lot of time to map a reasonable area and even the tapping mode technique has difficulties with very large surface defects.

The target was to be able to routinely check rolls and average the results from a number of different viewed fields. A non-contact technique was used that could be developed into a semi-automated system.

Using a standard optical microscope Incident Dark Field was the method used to view the defects. This technique had two drawbacks, it did not allow for discrimination between the different types of defects, because they all appear bright against a dark background, and the second limitation was that there was no indication of the height of the defect. The use of Differential Contrast Microscopy of the same area allowed these limitations to be addressed. The primary advantage of dark field microscopy was that it gave a good contrast allowing the digitized image to be automatically processed using Image Analysis. The minimum defect that could be reliably detected using Image Analysis was 4 pixels in size and above a certain size there were problems of signal saturation. Thus two magnifications were typically used when counting defects, 400x to show defects in the range 0.3 – 2.0 microns and then 300x for defects in the range 1.0 - 10.0 microns. The area used within the field of view was 170 x 170 microns. There can be a tendency, when examining surfaces, to move the sample around to get a more interesting view. The danger of this can be that the view used is not representative of the whole. To overcome this it was decided to average the results of six different views. The image analysis measured the maximum and minimum size of each defect and these dimensions were averaged.

Figure 4 shows a histogram typical of the output of the average contamination of the six random fields of view with the cumulative total of defects of 974.

One observation that resulted from this work was that the defect count doubled if the web was slit again. This is not too surprising as the web had another series of rollers with which to add more surface charge and the web was exposed to the contaminated atmosphere, including the slitting debris, for a second period of time.

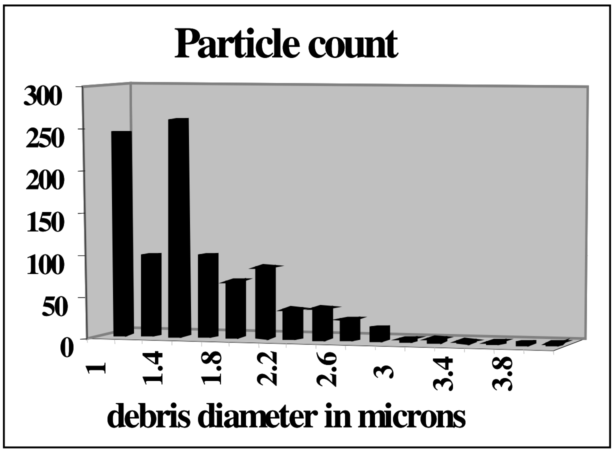

Figure 4. A histogram of the number and size of particles within the field of view.

Another observation was that the number of defects was worse approaching the final few turns before the core and on the first few turns of the roll. This would be where the web winding speed was either accelerating or slowing. The web near the core tended to be affected by the core type. Cardboard cores tended to have a higher level of debris on the web. Polymer sealed cardboard, polymer or metal cores were in general cleaner with the level of contamination being related to the quality of hygiene adopted.

The polymer or metal cores are easier to keep clean and generate little dust. However they are not without potential problems. The surface of the cores can be easily damaged such as by the simple act of cutting off the polymer web using a knife. If care is not taken it is common for the knife to score the core surface. These score marks may have a raised, sharp edge that can damage the next web that is wound onto the roll. Any damage can show through many layers in the wound roll.

Figure 5 shows a selection of some of the type of film tested. It is interesting to note that of the film samples tested the best film samples were made on low output specialist film lines and were expensive grades of film. Even the best sample was still 35x worse than was acceptable for the ODS application.

It is worth noting that when the magnification was increased to allow counting of defects below 0.3 microns the numbers were higher still. Thus for ODS where the target was to use shorter wavelength lasers the best substrate had at least a couple of orders of magnitude too many defects present before the coating process started.

Film Type	**Thickness**	**Mean diameter of defects**	**Number of defects**
	microns	microns	Average of 6 fields
SKC	23	2.5	2750
SKC	75	2.6	650
Upilex	75	3.1	36
Mylar D	23	2.6	400
Mylar D	75	2.6	600
Melinex 401	75	1.7	45-300

Figure 5. Some of the film samples tested.

SOURCE OF CONTAMINATION

As with many products the quality can vary between manufacturers depending upon many factors such as the age of the plant and the quality standards employed.

As polymer film is wound over rolls an electrostatic charge is built up on the polymer surface. This electrostatic charge will attract airborne particles to the surface. Unless these particles are removed they will be trapped between polymer layers as the web is wound into a roll. The debris thus contained within the roll may cause damage to the surfaces depending upon the tension used and the particle size of the debris. It is common for polymer webs, that are to be used in vacuum deposition systems, to have one side of the web given a controlled surface roughness to prevent the web from blocking during winding. If the debris is small enough then there will be little or no pressure exerted on the debris. Larger particles will be pressed into the surface and may just dent the surface or they may be pressed in deeper and become deeply embedded into the surface.

Many of the newer applications using polymer webs take great care to minimize contamination during manufacture and coating processes are often carried out in cleanroom environments. (Ref. 4) Typically polymer webs are not manufactured in a cleanroom. The manufacturing process includes activities that generate debris and hence the cleanest manufacturing conditions are on the first day of manufacture. As time goes on the manufacturing environment is likely to decline in quality due to accumulation of debris. This contrasts with the applications where the requirements for cleanliness are getting more stringent with time.

It was observed that the debris on the surface was not consistent and when it was investigated further it was found that the contamination levels were seasonal. The contamination peaked when the pollen count was high.

Looking at the manufacture of Polyethylene Teraphthalate (PET) there are two major points where debris can be generated. Within the stenter ovens some of the unpolymerised polymer will be vaporized into the hot air within the ovens. This monomer vapour may be condensed out onto cool surfaces producing a white powder or ‘snow’. This powder accumulates and may be disturbed by the circulating air and much may end up depositing on the polymer web.

In some cases the air is filtered as it recirculates. Filtering can be difficult, if the filters are too fine they limit the airflow and if they are too coarse they do not remove enough of the debris. A system was built using a system that uses the air only once however this was a high cost option, the cost of heating the air and maintaining the film temperature significantly increased the manufacturing cost.

The second significant source of additional contamination is from the slitting operations. The web as it leaves the stenter has the edges that were held by the stenter clips slit off. The slitting process generates debris and this is done adjacent to rollers that are charging up the polymer surface. In fact the polymer acts as an electrophoretic pump reducing the debris in the atmosphere by collecting it onto the polymer web.

PREVENTION AND CLEANING

It is first worth noting that cleaning is a fix not a cure. The ideal would be to not allow contamination in the first place thus making cleaning unnecessary.

It is probably unrealistic to expect to enclose the whole of a film line in a cleanroom however it is possible to use clean hoods with controlled filtered laminar flow at critical points to minimize the contamination from airborne debris.

There is a global trend that shows that as cutting processes are improved they go through various process steps from mechanical cutting through flame, plasma, water jet and ending up with laser cutting. The laser cutting is a finer and cleaner process than cutting with blades producing less edge damage and debris. Using laser slitting combined with localized vacuum extract and static neutralization it is possible to minimize the contamination from the slitting process.

Reducing the contamination within the stenter is more difficult. The ideal would be to use air for a single pass so that the white powder is continually swept away. A cheaper alternative could be to use electrophoretic collectors within the space to better collect the powder in conjunction with filters. This would require more frequent cleaning that would also add to the cost.

Another approach that is being used on some bubble lines is to allow the web to become contaminated and to then clean the web immediately before winding it into a roll.

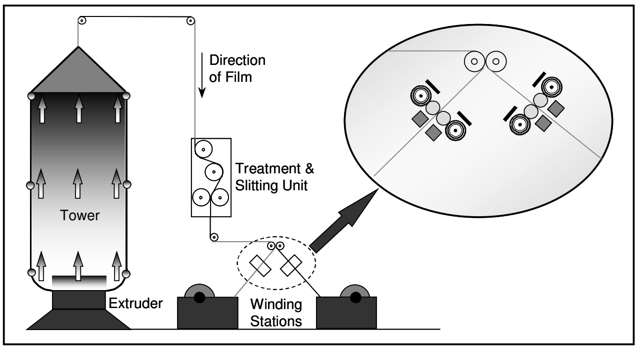

Figure 6. A schematic of a bubble process with the cleaning tack roll sited immediately before the rewind. Ref. 5

The technique used for this is to use a tack transfer roll to which the debris adheres. The transfer roll then contacts a high adhesive collection roll that accumulates the transferred debris. This technique has advantages over air knives and ultrasonic pulsed air jets with anti-static bars and vacuum extract in that they can more easily penetrate the air boundary layer. The boundary layer is a problem, particularly at higher winding speeds. This technique is claimed to remove all debris down to <0.3 microns reproducibly.

This technology is used by flat screen television manufacturers immediately prior to laminating the multilayer contrast enhancement filters onto the front surface of the screens.

This technique would not only need to be applied to the manufacturing line but also to the offline slitting machines.

This technique is by far the cheapest to install onto a web production line but is a fix and not a cure.

One process commonly used in vacuum systems is plasma cleaning. In this process the plasma will remove any static charge allowing some of the debris to fall off due to gravity or if the particle gets charged it may be ejected into the plasma. Again this does not remove all of the debris and by itself is insufficient.

There is a limit to how fine the particles are that can be removed by these techniques. It has been said that for debris below 0.3 microns the Van der Waals forces holding the particle onto the surface are such that it would require a crowbar to remove each one. Thus the removal efficiency decreases with decreasing size of particle.
Hence it may be that no matter how much cleaning is done the surface can never be cleaned sufficiently well to meet the requirements and other solutions need to be adopted.

A concern that arises from the use of very smooth, flat and clean surfaces is that they are difficult to wind, particularly in vacuum. It is common that the back surface will either be coated or have fillers to make small bumps on the surface to help minimize the polymer to polymer contact allowing easier winding by preventing the frictional adhesion of the polymer surfaces known as blocking. An alternative way that this can be overcome without worsening the surface quality is by using edge knurling. Knurling is where a regular embossed pattern is added usually to the roll edges. The raised profile of the knurl takes the load and allows the surfaces to be wound with minimized contact. This prevents the problems of blocking. Care needs to be taken in producing the knurl. The traditional method of producing a knurled pattern is to use knurled rollers and apply pressure to the roll to the point where the polymer flows and the pattern is produced. It is possible that this can also produce debris. The knurled rolls can act like cutters and cut the pattern into the surface and in doing so debris is generated. It is possible to use a pulsed laser to produce a raise pattern that is a more controlled and reproducible process but is more expensive to install.

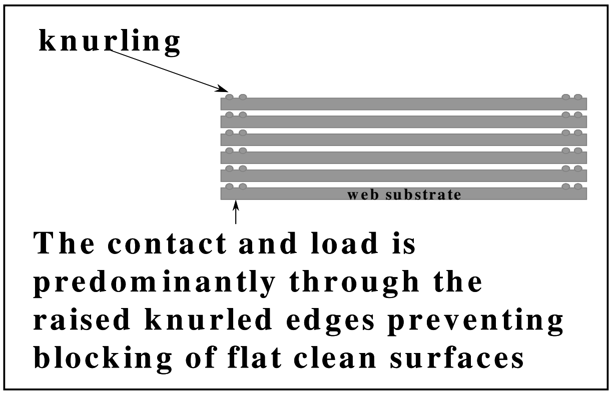

Figure 7. A schematic of a knurled roll of polymer.

ALTERNATIVE STRATEGY

The alternative strategy, already adopted by some, is to not clean off the debris but to coat the surface with a polymer to a thickness that will cover up all of the debris. There are two options for this coating one is to deposit the coating whilst the web is at atmospheric pressure and the second is to deposit the coating in the vacuum system.

If this coating is done at atmospheric pressure then not only does the polymer need to be finely filtered but also the surface needs to be protected from being re-contaminated from the atmosphere after the coating process. This is pushing the cost of clean air laminar flow cabinets from the web supplier to the web user.

If the coating is applied under vacuum the vacuum system acts as a cleanroom as the bulk of the airborne contamination is pumped out along with the air as the vacuum is produced. This process also allows the vacuum deposited coating to be applied immediately after the polymer coating and the opportunity for contamination is minimized.

Depositing solvent or aqueous coatings and drying them could be difficult for such thick layers. In particular drying off either in vacuum is not practical. This would tend to lead towards the UV or e-beam cured polymeric coatings or hot-melt type technology.

The process of applying polymers via a spray and flash evaporation source and e-beam curing is patented and well documented and is being used to develop the ultra high barrier coatings required for OLEDs. (Ref. 6)

As there is now the situation of having to coat the web with a polymer to achieve the desired surface performance the situation could be envisioned where a much cheaper thinner web substrate is used and the applied polymer coating is used to provide more of the desired performance. This could enable more complex multilayer polymer coatings to be used to provide a variety of different attributes. Thus instead of using a 5 mil (125 micron) substrate a 1 mil (25 micron) substrate could be used with the other 4 mils (100 microns) applied as part of the coating process.

Having plenty of thickness to work with could allow refractive index matched layers to be used to more easily in multilayer stacks to produce a complete optical package rather than adopting some of the compromises normally associated with trying to minimize the number and thickness of coatings. A schematic of a possible structure is shown below.

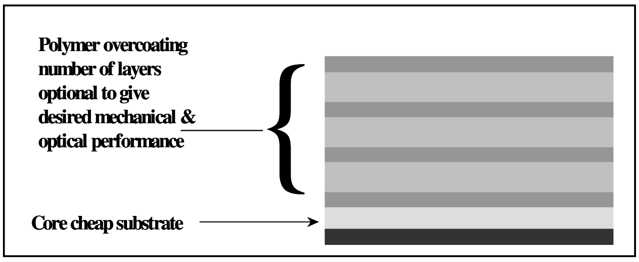

Figure 8. Potential alternative substrate using low cost substrate and adding functional coatings.

CONCLUSION

There are a number of actions that could be taken by polymer manufacturers to produce cleaner films. There is an opportunity for one of the manufacturers to become the leading cleanest web producer. However unless their customers can collectively exert enough pressure on the manufacturers it is unlikely that this type of investment will be made and none of the necessary actions will be taken.

Even if these actions are taken it is likely the web will still not be clean enough for some applications and additional action will need to be taken by the web users. The simplest method to produce the required surface quality is to add a coating thicker than the surface contamination immediately prior to the vacuum deposited coating.

If the investment in cleaning and coating process has to be made then it is an option that these processes be developed to enable cheaper web to be used. Utilizing their own coating process to add the required functionality rather than paying a premium for web and still having to coat it before use.

An extreme version of this would be to use the minimum gauge of web and add thicker and possibly multiple coatings to obtain better optically matched products with fewer optical compromises.

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