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Coating improvements through better control of water vapour in vacuum deposition

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Abstract

Water is the dominant species in most vacuum systems. It is well known that cryo-surfaces can significantly speed up coating processes by efficiently removing water and shortening evacuation times. The improvements in coating quality are less well known. Contamination of thin films by background water in the vacuum alters their mechanical, electrical, optical and chemical properties. This paper discusses the advantages in coating performance that users experience with efficient removal of water from their vacuum systems.

The best method of incorporating water vapour cryo-surfaces into a web coater is also discussed. We show that the best deposition chamber vacuum is obtained by splitting the cryo-surface into two and placing half in the deposition chamber and half in the winding chamber.

Introduction

Water vapour cryo-surfaces are essential for economic vacuum metallizing. It is well known that they reduce the pump out/cycle time. Here we will review the evidence that by improving the vacuum they also have a strong effect on the film properties.

For metallized webs there is evidence that improved vacuum leads to improved web properties (optical density, oxygen barrier properties and uniformity). There are also new higher value products appearing whose production requirements go beyond metalized webs :-

- Optically Variable Devices (OVDs)
- Ultra barrier coatings for displays and batteries

OVDs and holographic foils contain optical layers which require precise thickness and refractive index control. Ultra barrier coatings require precise control of the mechanical properties. These new requirements for web processing mean that the vacuum environment needs improved control.

Pump out times

The typical reason for adding a water vapour cryo-surface is the dramatically increased pumping speed that they offer. This is very cost effective as pump out times are reduced, saving valuable coater time and increasing production. The example shown here is from another high gas load application - vacuum welding (ref. 1). In this application when a water vapour cryo-surface is added then the main pumps can be turned on 30 minutes earlier and the working vacuum pressure (10^{-3} mBar) is a achieved almost an hour earlier.

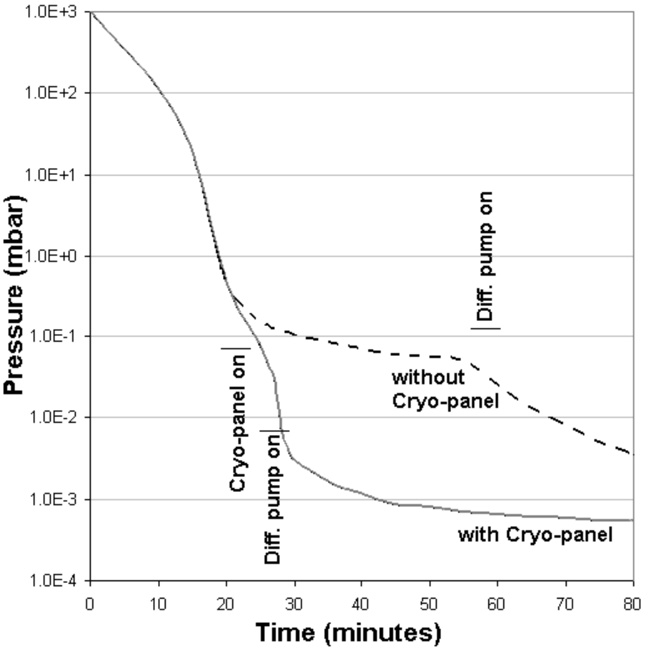

Figure 1 : Reduced pump out times and improved vacuum levels when a water vapour cryo-surface is used (ref. 1).

Metallizing

As well as reaching vacuum faster, web coaters with water vapour cryo-surfaces also reach improved the vacuum levels. The barrier properties of metallized webs are improved by operation at better vacuum levels. Eldridge Mount highlights this in one of his 'Ask AIMCAL' answers (ref. 2). Experiments on a web coater showed that as the chamber pressure was allowed to rise from 1 x 10^{-4} to 1 x 10^{-3} Torr then the optical density dropped from 3.0 to 2.4. The oxygen permeation rose from 2.5 cc/100inch^2/day to 14.5 cc/100inch^2/day. This was not simply due to the drop in O.D., with good vacuum an O.D. of 2.4 oxygen permeation should give oxygen permeation of only 4 cc/100inch^2/day (ref. 3).

The conclusion from this is that*'Chamber pressure is a critical parameter in determining important barrier properties of metallized film products. As vacuum-chamber pressure rises, the many process changes needed to compensate for it may generate other product changes, lowering film quality and overall productivity.'* (ref 2).

The same experiments also found worse coating uniformity at the higher chamber pressures (ref 3).

Background information

In other coating areas it has been shown that even small concentrations of water or water products (O, -OH, H) can have significant effects on coating properties.

Ishibashi et al showed that a water pressure of 2 x 10^{-5} Torr during sputtering had significant effects on both the resistivity and etching properties of the conducting transparent oxide ITO (ref. 4). Also on ITO, Lee at al found changes in the crystal structure (sizes and lattice constant) and electrical properties as they varied the base pressure between 2.5 x 10^{-7} Torr and 2 x 10^{-5} Torr, for films deposited at 5 nm/s by sputtering (ref. 5).

Schneider, Anders et al found that both arc evaporated and sputtered Aluminium Oxide films could contain significant amounts of hydroxides and that the background water pressure caused this. They believe that this causes the wide range of refractive indices and chemical stability reported for thin film Aluminium Oxide (ref. 6). The same group (Schneider, K. Larsson, et al) later found alterations in the mechanical properties of Aluminium Oxide thin films caused by the water vapour in the vacuum (ref. 7).

Schneider, Hjorvarsson et al also found significant OH content in sputtered Strontium Titanate films (up to 8%). This material is of interest for electronic device applications because it has a large dielectric constant and high breakdown strength. This incorporated OH reduced the dielectric constant (ref. 8).

Security and Anti-Counterfeiting Devices

In the high growth area of security and anti-counterfeiting high refractive index coatings (HRIC) are used to boost the reflection but maintain sufficient transparency to view the protected document (refs. 9, 10, 11). The requirements now include more precise thickness control as the wrong coating thickness can produce unwanted colours or too low a reflection (ref. 12). Of the high index materials available (ZnS, TiO2, etc., ref. 9), most of the work has been on ZnS because this can be made at higher speeds. Similarly a variety of production methods are possible (vapor deposition, sputtering, reactive sputtering, ion plating, electroplating, etc., ref 11), but vapour deposition is favoured because of the higher production speeds.

Roll speeds of about 1500 fpm can be achieved for ZnS; however pressures of about 10^{-5}

Torr are required (ref. 13). This is a substantially better vacuum than that achieved in a 'typical' web coater (ref. 14).

Barrier coatings

Ultra barriers are a new potential market for organic displays. These display materials are very sensitive to moisture and oxygen. Currently development is on glass substrates but there is a large demand for flexible displays. This will require transparent, ultra-barrier coated polymer webs.

Many potential barrier materials include Nitrides (ref. 15). If reactively deposited, nitride coatings will be prone to unwanted oxides or hydroxides or hydrides from the background water vapour, this is because these unwanted water species are much more reactive than nitrogen.

Metal Oxides such as Si, Al, or Mg oxides are also promising barrier materials (Refs. 16, 17). Evaporation of these barrier layers suffers from coating thickness errors caused by changes in the coater vacuum (ref. 17). Toyo deal with this by an X-ray fluorescence in-situ thickness measurement to measure and control the coating thickness (ref. 17).

Achieving the required pressures

We have shown that chamber pressures in the 10^{-5} Torr range are required for coated web products more sophisticated than simple metallized webs and that even metallized webs benefit from improved base pressures. Web coaters without water vapour cryo-surfaces only give pressures of the order of 10^{-4} Torr (ref. 14). Adding a water vapour cryo-surface typically gives pumping speeds of around 200, 000 l/s and significantly improves the vacuum but where do we place the pumping coils ?

We have used the model and values of Keiser *et al* (ref. 14) for a 650 mm wide web but modified it to include a water vapour cryo-surface. Figure 2 shows a schematic of a two chamber web coater. We have calculated the winding chamber pressure as

$$P_W = Q_W/S_W$$

where

Q_W = gas load into the winding chamber from the web
S_W = winding chamber pumping speed.

We have used a value for the gas load Q_W = 80 Torr.l/s which corresponds to around a $1m^2$ area of polyester. The deposition chamber pressure is calculated as

$P_D = (Q_D + Q_{W \rightarrow D})/S_D$

where

Q_D = gas load from the deposition chamber

$Q_{W \rightarrow D}$ = gas load into the deposition chamber from the winding chamber

S_D = deposition chamber pumping speed.

The gas load from the deposition chamber itself is taken as 0.5 Torr.l/s. The gas load into the deposition chamber from the winding chamber is calculated as the product of the conductance between the two chambers and the differential pressure. The inter-chamber conductance $C_{W \rightarrow D}$ is taken as 220 l/s.

$$Q_{W \rightarrow D} = C_{W \rightarrow D} .(P_W - P_D)$$

We have used conventional pumping of 10,000 l/s in both the winding (S_W) and deposition (S_D) chambers. A water vapour cryo-surface of 200,000 l/s is then added to the Keiser model and we have calculated the deposition chamber pressure for various coil placements.

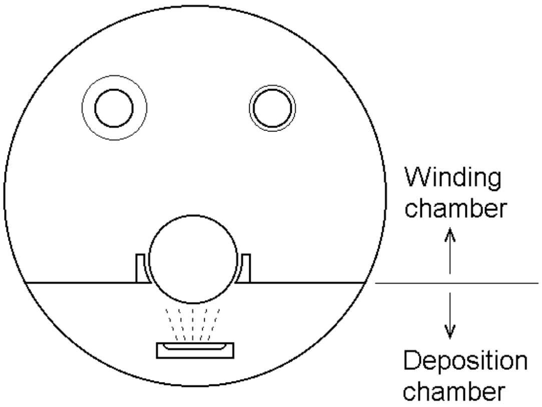

Figure 2 : Web coater schematic for deposition chamber calculation (after Keiser *et al*, ref. 14)

Table 1 : Calculated deposition chamber pressures for various cryo-surface placements

		Cryo-surface in Winding Chamber	
		NO	YES
Cryo-surface in Deposition chamber	NO	2.3 x 10^{-4}	5.8 x 10^{-5}
	YES	1.1 x 10^{-5}	6.0 x 10^{-6}

Note : the 200,000 l/s coil has been split into two 100,000 l/s sections for the calculation of a coil in both winding and deposition chambers.

This calculation shows that the most efficient placement of the water vapour cryo-surface, is to split the 200,000 l/s coil into two and place a 100,000 l/s coil in each chamber. Compared to the typical cryo-surface placement in the winding chamber this should give roughly an order of magnitude better vacuum in the deposition chamber. The additional cost will be minimal as it will simply be for extra feedthroughs and chamber holes, while the same compressor/chiller can be used to power both coils (as the total coil size is not increased).

A leading UK based web coater Ultimet Films placed a second cryo-coil in the deposition zone of their Valmet / Vacuum General EHF2050 system for coating of 2m wide webs (ref. 18). Ultimet Films' experience has demonstrated to them that a water vapour pump coil in the deposition zone was crucial for two main reasons:

1. Over a period of time, Aluminium Oxide powder built up on the chamber walls, evaporation trough and shutter in the vicinity of the Aluminium Deposition Source. Aluminium Oxide absorbs moisture readily. During the reel turn-around period, moisture from the air absorbs into this Aluminium oxide layer. This is particularly pronounced in areas of high humidity, where greater uptake of moisture has been noticed.

2. Without a cryo-coil in the evaporation zone, moisture in the Aluminium Oxide powder outgases resulting in extended pump down times. A pump down time may

be extended by 15-30 minutes depending on the film being processed. The effect of water vapour on film quality can be demonstrated by switching off the Water Vapour pump, moisture vapour is then not collected on the coil. A certain amount of water vapour is removed from the powder during the pump down. However a much greater amount is released when the heat load from the evaporators drives out the final amounts. This creates a pressure rise in the deposition zone which leads to “Bronzing” of the coated film. Running speeds must also be reduced to achieve the set optical density. In the opinion of Ultimet Films it is essential to have a coil in the evaporation zone to minimize these problems.

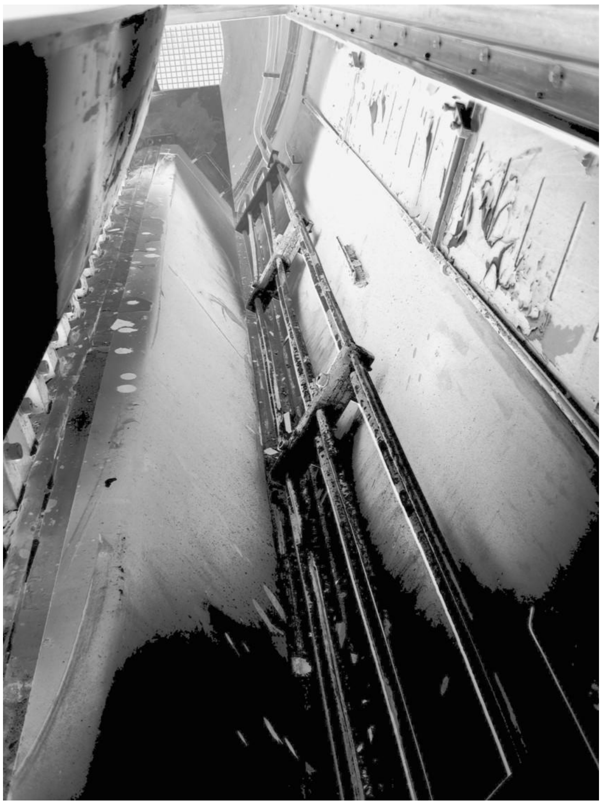

Figure 3 : Cryo-coil located in a Valmet EHF2050, 2metre wide web Coater (ref. 18)

Some films such as Cellophane have a high water content of up to 5%. During the metallizing process, the Aluminium heat load on these films can cause out-gassing of water vapour. Again without a cryo-coil in the evaporation zone, bronze coloured film and poor metallization appearance can result.

It was also found that placing a water vapour cryo-coil in the deposition zone improved deposition consistency across the web width. This is thought to be due to the improved vacuum levels and uniformity at the point of deposition.

Conclusions

It is known that water vapour cryo-surfaces greatly reduce vacuum pump-out times but by improving the vacuum level in web coaters they also lead to improvements in coating quality. Poor vacuum levels lead to unwanted contamination of coatings with oxides, hydroxides and hydrides. We have reviewed the literature and found many instances where this contamination changes the coating properties and reduces the coating performance.

The best placement of the cryo-surfaces in the web coater was investigated with a simple model. Typically water vapour cryo-surfaces are placed in the winding chamber with the logic that this is where the highest gas loads occur. Our calculation shows that an order of magnitude improvement in the deposition chamber vacuum can be achieved by splitting the cryo-surface into two separate coils, each of half size. One coil is placed in the winding chamber, the other in the deposition chamber. This order of magnitude improvement can be achieved at minimal cost.

Practical experience at Ultimet Films shows the benefit of this cryo-surface in the deposition chamber both in terms of pump out speed and coating quality.

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