Thin Film Slot Coating in a Rarefied Low Viscosity Gas

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Requirements for a Typical OPV (Organic Photo-Voltaic)

Background figure courtesy Bjorkland, G.C. and Baer, T.M. “Organic Thin-Film Solar Cell Research Conducted at Stanford University” Photonics Spectra Nov. 2007, pp 70-76.
Typical Limitations using Slot-over-Roll Coating
Lee,K-Y; Liu L-D & Liu,T-J [1992]

Effect of Coating Gap H on Minimum Wet Thickness for Conventional Extrusion Slot Coating
50mPa.s Silicone Oil - 0.25 mm Slot Gap
X denotes maximum coating speed

e.g. Q = 1 cc/s
“Old” Methods to reduce film thickness & increase speed in slot coating

1. **Bead Vacuum**: reduces minimum film thickness by more than 30% when it is sufficiently high. See Lee et al. Chem. Eng. Science, *47* (7) [1992]. Mechanism: coating bead is pulled back & downstream lip serves as a doctor blade & restricts net flow.

2. **Tensioned-web slot coating**: Dispense with backing roller and allow the gap to be reduced further without danger of clash between slot and steel roller. Films as thin as 0.5 microns can be produced but only at very low speeds, typically less than 10 m/min.
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Motivation for our work: aim to achieve thinner layers at higher speeds with added advantage of prolonged end-product life by coating in an oxygen-free atmosphere
REPLACING AIR WITH HELIUM AND REDUCING THE PRESSURE SIGNIFICANTLY ENHANCES THE MAXIMUM COATING SPEED FOR DIP COATING

Why should helium be more effective than air or CO₂ when reducing the pressure?

![Image of a tank containing silicone oil](https://via.placeholder.com/150)

tank containing silicone oil
1. The higher the viscosity of the gas, the greater the coupling force between the gas and the liquid, the more the gas will be dragged down by the web.

2. Low viscosity gas exerts less coupling force on fluid and hence reduces size of vees and delays onset of gas entrainment.

Viscosity measured between surfaces several mm apart fails to explain results.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Bulk viscosity at 20°C and 1 atmos.</th>
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<tbody>
<tr>
<td>air</td>
<td>181 µP</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>149 µP</td>
</tr>
<tr>
<td>helium</td>
<td>199 µP</td>
</tr>
</tbody>
</table>

\[ \eta = \frac{2}{3\sigma^2} \sqrt{\frac{mkT}{\pi^3}} \quad \text{hence} \quad \eta \neq (P) \]
Viscosity of a gas remains almost constant as pressure is reduced until mean free path approaches linear dimensions of measuring apparatus.

But Mues, Hens and Boiy [1989] found that air entrained at coating constrained to films typ. < 5\(\mu\)m thick.

So we need a measuring apparatus where solid boundaries are typ. 2\(\mu\)m apart.
One plate set in oscillation in direction normal to other spring loaded plate – measure relative motion and hence damping

master curve for dry air, argon, N₂, A, CO₂, O₂ and H₂

\( d = \text{gap} \quad \lambda = \text{mean free path} \)

Plausible explanation for why helium performs well for dip coating

So will it also benefit slot coating?
Challenging expts requiring developing miniature parts, controlled ramping-up and down web speeds+ tricky imaging optics/cameras/ SYNCRO-RECORDING

SLOT-OVER-ROLL MODE

Coating Fluid: Silicone oil, $\mu = 50\text{mPa.s}$

Film thickness measured using a capacitive sensor supplied by Physik Instrumente GmbH

gravity feed

speed ramped up at constant acceleration to save base + oil
TENSIONED WEB SLOT COATING MODE

Head withdrawal facility to avoid excess fluid draining down web at start-up

Slot / bead visualised using INFINITY zoom + std. objective set up to view through the web

Oil fed using micro-pump to achieve lower flow rates / film thicknesses – problem with cavitation bubbles
PARAMETERS
Slot exit = 0.425 mm x 4.5 mm  Web width = 5 cm
μ = 50 mPa.s  σ = 17.9 mN/m  ρ = 985 kg/m³

SLOT-OVER-ROLL
Upstream land length = 0.2 mm
Downstream land length = 1.5 mm
Coating gap = 0.20 mm

TWSC MODE
Web spans:
7.5 cm upstream
10.2 cm downstream
Web deflection = 2 mm
Upstream land length = 1.5 mm
Downstream land length = 0.2 mm
Web tension = 4.3 N
Four cameras used to display and record web speed, movement of coater from withdrawn to coat position, onset of entrainment/ribbing and flow rate.

- Web
- Side view of slot coater
- Coating speed
- Micromanometer displays flow rate
- Air/gas entrained at dwl
TYPICAL RECORDINGS - SLOT-OVER-ROLL

Coating Speed Profile

Coating Thickness vs Time

coating speed at onset of air entrainment

optical tacho O/P

wet thickness at onset of air entrainment

capacitive sensor O/P
RESULTS - SLOT-OVER-ROLL MODE

Results for air at atmos. pressure match those of Lee et al. [1992] quite well.

Replacing air with He at low pressure reduces wet thickness by typically 17%.
Replacing air with He at low pressure reduces Hmin for given U by typically 50% or can increase Umax by >>2x for given H
CONCLUSIONS

• Replacing air at atmospheric pressure with helium at low pressure significantly reduces the low wet thickness limit or alternatively increases the coating speed for a given wet thickness for both slot-over-roll and TWSC configurations
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- Problems due to bubbles in the supply line at low pressures and the need to refine the measurement of thin films to be resolved.
ACKNOWLEDGEMENTS

• We gratefully acknowledge the help of Physik Instrumente GmbH who kindly made available their capacitance probe system to measure wet film thickness without which these experiments would not have been possible