What I’ll Cover:

• Intro To Camvac and its place in the History of In Vacuum Metallisation.
• Brief Background on In Vacuum Polymeric Coating:
  • IVC: What is it?
  • IVC: What has been Developed
• Where IVC is Different:
• Camvac’s Journey:
  • Early Days.
  • Chemistry.
  • Key Problems Faced.
• Unit Design:
• Process Today:
• Why / Benefits: (was it worth it)
Camvac: Our Company

- **Location:**
  - Thetford, Norfolk, UK

- **Employees:**
  - ~ 133 employee

- **Area:**
  - 5.2 acre site

- **Capabilities:**
  - Metallising (4x Production Metallisers)
    - 2x 2250mm; 1x 2180mm; 1x 1650mm
    - 2x AlOx (Camclear); 1x Double Coat; 1x IVC
    - Dev Metalliser (450mm: AlOx; IVC; Other Metals)
  - Lamination (2x 2250mm Laminators)
    - R1 – Triplex: Solvent Based & Thermal; Lacquering & Single Colour Printing
    - R2 – Duplex: Solvent Free
  - Slitting (5x Slitting Machines)
Camvac: Our History in Vacuum Metallising

• 1950s – Messrs, Nissen and Cookson:
  – Vacuum research & research into metallising.
  – Built first ever metallising machines.

• 1960s – Moved to Thetford:
  – Started metallising as commercial process.

• 1970s – Barrier Discovered:
  – First metallised laminate for a barrier food pack.

• 1980s – Lamination:
  – Met OPP and Paper.

• 1990s – Camclear®:
  – First company in Europe to develop AlOx Metallisation process.

• 2000s – IVC:
  – Developed in vacuum polymeric coating technology.

• 2010s – Today:
  – More focus on Specialities.
  – Very high barrier laminates for specialist markets.
Brief Background on In Vacuum Polymeric Coating:

- Interest in in vacuum polymeric coatings dates back as far as the late 1970’s / 1980’s.
- Numerous pieces of IP covering: Processes; Products and Chemistries.
- Additionally a number of presentations at the likes of SVC and AIMCAL have been given over the years.
- A lot of work has focussed on the deposition and curing of acrylates for improved performance of barrier films.
- Although some commercial systems have been sold, until recently there has been very little commercial product reaching the market made using such systems.
- Why?

PAIN

- Certainly this has been Camvac’s experience.
Camvac’s IVC (In Vacuo Coating) Process:

- Organic Monomer (typically an acrylate) is fed into Delivery Unit.
- Flash vaporisation of Monomer at ~250 °C.
- Monomer Deposited onto Moving Substrate (typically a polymer web).
- In line barrier layers added either Pre and or Post IVC coating.
## IVC: What has been Developed

During IVC development 3 Key strands were followed:

### Planarising Layers:
- **Camplus Extra**: Al Barrier
- **Camclear Extra**: AlOx Barrier

### Polymer Multi-layers (PML’s):
- **Camquest**: Al Barrier
- **Camclear Quest**: AlOx Barrier

### Protective Top Coats:
- **Camshield M**: Al Barrier & IR Control
- **Camshield T**: AlOx Barrier

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>Material</th>
<th>Development Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planarising Layers</td>
<td>Al Barrier</td>
<td>Commercial Products in market</td>
</tr>
<tr>
<td></td>
<td>AlOx Barrier</td>
<td>Pilot Scale Only – Still under development.</td>
</tr>
<tr>
<td>Polymer Multi-layers (PML’s)</td>
<td>Al Barrier</td>
<td>Some commercial sales but development still ongoing.</td>
</tr>
<tr>
<td></td>
<td>AlOx Barrier</td>
<td>Little development only recently started.</td>
</tr>
<tr>
<td>Protective Top Coats</td>
<td>Al Barrier &amp; IR Control</td>
<td>Commercial Products in market</td>
</tr>
<tr>
<td></td>
<td>AlOx Barrier</td>
<td>Commercial Products in market</td>
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</tbody>
</table>
Where IVC is Different:

- **Curing:**
  - Instead of e-beam or UV curing Camvac, alongside John Topping (MFN Technologies), developed Plasma curing.
  - Polymeric (Acrylate) coating is cured by either:
  - Where the electron or ion flux is generated by low pressure gas plasma.

- **Thickness of Coating:**
  - Many coatings are in the 100’s nm to µm thicknesses.
  - IVC coatings are ~50nm thick

- **Site of Vaporisation:**
  - Many systems vaporise the monomer externally to the chamber and is piped to the delivery head. In IVC system vaporisation occurs within the delivery head.
Camvac’s Journey: Early Days

- **1990’s:** Initial trials conducted with Catalina Coatings, Sigma Technologies and Galileo (EB curing)
- **2001/02:** Ideas/discussions/thoughts etc. look-see at a machinery manufacturer.
- **2003:** Early investigations with the late Bernard Henry at Oxford University (EB polymerisation).
- **2005:** Regular trials at Oxford Uni.
- **2006:** Breakthrough on adhesion – Mix 1.
- **2007:** Collaboration with John Topping (MFN Technologies) Started looking at Plasma polymerisation.
- **2007/08:** Development brought “in house” at Camvac.
- **2008:** Commissioning new Pilot Line at Camvac (I join Camvac).
- **2008-09** Development of process on pilot line.
Camvac’s Journey: Chemistry

- Early trials at Oxford mainly focused on PML structures and using a cured acrylate as an interlayer between two Al Met layers:
  - Using TPGDA (Tripropylene Glycol Diacrylate).
  - Barrier was excellent (<0.1 cc/m²/day and <0.1 g/m²/day).
  - Adhesion very poor (often <10g/25mm).
  - Even as a planarising layer adhesion poor (<50g/25mm).

- Started looking at alternatives:
  - Early breakthrough after speaking to acrylate supplier – Mix 1
    - 3 Component comprising:
      - 2 Active Components
      - Acidic adhesion Promoter

- Still Problems:
  - Odour
  - Some Adhesion Issues remained
  - Viscosity – Not easy to pump

- Quest Continues
Camvac’s Journey: Chemistry

- 100’s of Separate Runs on Dev Line
- >1000 MVTR Tests
- >1000 OTR Tests
- 1000’s of EAA & Adhesion Tests
- Many, Many Hours
- At Last count Over 200 Acrylate Mixes Made

Over 200 Acrylate Mixes Made
Camvac’s Journey: Chemistry

• **Outcome:**
  • Current Mix = Mix 1C
  • Based on early Mix 1 but refined and simplified.

• **What have we learnt? Acrylate Needs:**
  • Show Barrier Improvement Barrier:

   • **Adhesion / Cohesion:**
     Ideally >300g/25mm in whatever structure it goes into.

   • **Wetability:**
     • Required to achieve good continuous coverage.
     • Poor Barrier and adhesion often a result of an acrylate mix not wetting well on the substrate.

   • **Flexibility:**
     • Required to prevent cracking.
     • Hard brittle acrylates tend to crack and sheer especially in thin ~50nm coatings.
       • Defects / Barrier loss.
       • Poor Adhesion.
Camvac’s Journey: Problems – Pumping Acrylate

• Syringe Pump:
  • Ok for early pilot trials.
  • Viscous acrylates an issue.

• Peristaltic Pumps:
  • Hard to measure delivery.
  • Delivery rate changed with viscosity.

• Micro Gear Pumps:
  • Better but accurate control still an issue.
  • 300 cP on edge of what they could handle.
  • Sheer forces in pump caused acrylate to “part polymerise” that could cause: - Jamming up, Broken Gears & Pump failure.

• Micro Gear Pump with Coriolis Flow Control:
  • Feedback allowed flow rate to be accurately controlled.
  • Didn’t overcome the issues of pump failure.

• Screw Drive “Visco” Pump:
  • Drive had to be calibrated to delivery.
  • Finally works well for viscous acrylates.
  • Reliability seems Good (>6 Months on Production machine – No issues)

Viscosity of Mix1 & Mix1C
~ 300 cP
Camvac’s Journey: Problems – Injection Nozzles Blocking

- **Early Injection Nozzles Could be prone to blocking:**
  - Cause acrylate to leak out elsewhere.
  - Particular issue on short runs – Development.
  - Caused Significant down time to clean / replace.
  - In production nozzles had to be regularly checked / replaced to prevent issues.

- **Solution:**
  - Multi way valve that allows the nozzle to be purged with gas at the end of run:
    - Prevents nozzle blockage.
    - Reduces build up of acrylate in boiler.
Camvac’s Journey: Problems – Fouling of Cure Plasma Units

• Early delivery issues could result in a large slug of acrylate exiting from the boiler. This could condense on the curing plasma unit, carbonise and cause fouling.

• Overcome by:
  • Tighter control on acrylate delivery.
  • Carful arrangement of plasma to delivery.
  • Removing water cooling off anode.
  • Careful selection of correct curing power.
  • Development of alternative plasma system – Plasma Roller.
Camvac’s Journey: Problems – Distribution

- **MD – Drip from Nozzle – MD Pulsing:**
  - Only an issue at low flow rates – Pilot scale.
  - Production scale – Less Issues:
    - Multiple Injectors
    - Higher flow rates

- **TD – IVC Nozzle Slot Fouling**
  - Acrylate could cure in nozzle slot.
  - Caused blockage at that point and stripe of thin / no acrylate on reel.
  - Overcome with:
    - Improved Internal boiler design.
    - Mk VII Unit – Allowed slot plate to be removed and cleaned.
IVC Unit Design: Early Models

Mk I / II (2006-2008)
• Vary small Proof of Concept Devices
• Blocked very quickly after 10’s of meters of delivery.

Mk III (Late 2008)
• Used 2x MkII units as a head with a larger feeding boiler.
• Allowed 100’s / 1000’s of meters material to be made at pilot scale ($\leq 450$mm).
• Electrically heated:
  – Cartridge heater issues.
  – Long heat up and cool downs.
Mk IV (2009)

- **First production width system (2200mm).**
- **Based on MkIII**
  - Nozzle made of multiple Mk II type heads side by side.
    - Heads expanded differently and warped causing major distribution issues.
  - Still Electrically Heated:
    - Boiler heating great.
    - Thermal expansion caused issues with heater elements on the nozzle heads causing them to blow.
  - Cool down very slow - no active cooling.
IVC Unit Design: Mk V

Mk V (2009-2010)

• Second Production Width System

• Attempt to rectify head warping issues of MkIV
  – Nozzle head now 1 single piece.
    – Distribution better but still not perfect.
    – Thermal expansion still an issue.
      – Heaters still blowing.
      – Cool down still very slow.

• Allowed first production width material to be made.
Mk VI (2011)

- **Single piece design with fixed nozzle slot:**
  - Distribution much better.
  - Nozzle would slowly block up in use.
    - Nozzle slot integral to boiler – Full strip down and reassembly required to clear nozzle slot.
    - 6-8h delivery before full strip down required.

- **Made of Al**
  - Good thermal transfer.
  - High amounts of thermal expansion.
  - In production proved to be insufficiently durable.

- **Oil heated:**
  - Heat up and cool down much quicker.
  - No issues of blowing heaters

- **Allowed first commercially saleable material to be produced.**
Mk VII (2013)

- **Adjustable / Removable Nozzle Slot Plate:**
  - Nozzle slot much easier to clean.
  - Some early distribution issues.
    - Overcome with clever internal boiler design.

- **Stainless Steel:**
  - More durable.
  - Easier Cleaning

- **Oil heated:**

- **Current Production System:**
  - 16h Strip & Clean Interval.
  - Quick change around.
IVC Process Today – System as Fitted in Our Production Machine

- Winding Chamber
- Metallising Chamber
- Unwind reel
- Rewind reel
- Lay on
- OD Check
- Metallising
- IVC Delivery Boiler
- Camplus pretreatment
- Camplus Cure

Camplus cleans the web, removes water and activates the surface prior to coating.

Coating applied free span.
Why / Benefits : SW Barriers

- IVC Planarising Layers & Top Coating give approx. 2 fold increase in SW barrier:
- PML Structures can give up to 1 order of magnitude improvement over single barrier layers.

<table>
<thead>
<tr>
<th>Barrier Structures</th>
<th>Typical OTR (cc/m²/day)</th>
<th>Typical MVTR (g/m²/day)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Met</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camplus Met (MPET)</td>
<td>0.60</td>
<td>0.50</td>
<td>Commercial Product</td>
</tr>
<tr>
<td>Camplus Extra (AM)</td>
<td>0.25</td>
<td>0.20</td>
<td>Commercial Products in Market</td>
</tr>
<tr>
<td>Camshield M (MA)</td>
<td>0.35</td>
<td>0.30</td>
<td>Commercial Products in Market</td>
</tr>
<tr>
<td>Camquest (MAM)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>Some Commercial sales but Dev ongoing</td>
</tr>
<tr>
<td><strong>AlOx</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camclear (AlOx)</td>
<td>3.00</td>
<td>2.50</td>
<td>Commercial Product</td>
</tr>
<tr>
<td>Camclear Extra (ACC)</td>
<td>1.00</td>
<td>1.50</td>
<td>Development only but Dev line found to be damaging barriers.</td>
</tr>
<tr>
<td>Camshield T (CCA)</td>
<td>1.50</td>
<td>1.50</td>
<td>Commercial Product</td>
</tr>
<tr>
<td>Camclear Quest (CCACC)</td>
<td>0.80</td>
<td>1.00</td>
<td>Development only but Dev line found to be damaging barriers.</td>
</tr>
</tbody>
</table>
Why / Benefits: SW Barriers

SW Met Barriers

- Typical OTR (cc/m2/day)
- Typical MVTR (g/m2/day)

Camplus Met (MPET)
Camplus Extra (AM)
Camshield M (MA)
Camquest (MAM)
Why / Benefits: SW Barriers

SW AlOx Barriers

- Typical OTR (cc/m²/day)
- Typical MVTR (g/m²/day)

Bar chart showing the comparison of Camclear (AlOx) and Camshield T (CCA) with typical values for OTR and MVTR.
Why / Benefits: Very High Barrier Laminates

Simple laminates of IVC structures to PE tend to show similar barriers to SW.

Multilayer Laminates with other materials able to produce extremely good barriers:

- OTR <0.005 cc/m²/day (<LOD of our equipment)
- MVTR <0.005 g/m²/day (<LOD of our equipment)

Above results have been verified by customers in their applications e.g. VIP's

Long tests required.
Why / Benefits: Barrier Retention

- IVC structures have shown much better barrier retention in end use application than conventional Met or AlOx barrier layers.

- E.g. Camshield T in Retort:

<table>
<thead>
<tr>
<th>Material</th>
<th>OTR cc/m²/day</th>
<th>Pre Retort</th>
<th>2h 121oC</th>
<th>3h 121oC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Competitor A</td>
<td></td>
<td>1.89</td>
<td>13.10</td>
<td>12.93</td>
</tr>
<tr>
<td>Competitor B</td>
<td></td>
<td>3.26</td>
<td>35.01</td>
<td>33.60</td>
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<tr>
<td>Camclear HB PET</td>
<td></td>
<td>1.64</td>
<td>3.56</td>
<td>2.08</td>
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<tr>
<td>Camshield T (Plain PET)</td>
<td></td>
<td>1.66</td>
<td>2.75</td>
<td>1.77</td>
</tr>
</tbody>
</table>

All above tested in exactly same laminate construction.
Why / Benefits: Barrier Retention

Camshield T vs Competitor Retort AlOx Films

- Pre Retort
- 2h 121°C
- 3h 121°C

OTR cc/m²/day

Competitor A
Competitor B
Camclear HB PET
Camshield T (Plain PET)
Why / Benefits: Improved Adhesion

- IVC layer as an under layer can be used to achieve excellent Metal adhesion on substrates where this can be challenging.  
  e.g.

  CPP

  - Without IVC Max ~ 200g/25mm
  - With IVC >500g/25mm achievable

- Has allowed materials previously considered un-metallisable to be metallised. (patent GB2500084)  
  e.g.

  Cellulose Acetate
Conclusions:

• It's been tough (PAIN).
• Been a few false starts.
• Many obstacles have been overcome.
• In Vacuo polymeric coatings do offer advantages:
  • Improved Barrier
  • Improved Adhesion
  • Improved barrier retention in demanding environments.
• IVC has allowed Camvac to develop new structures for new markets.
• There’s still plenty of room to improve.