Polymeric Coatings Overview

CHEM 550, Spring 2006
Ray Fernando, Cal Poly - SLO

- Coating Process – Life Cycle
- PVC, CPVC, NVV
- Chemistry, Function of Ingredients
- Coating Types – Waterborne, Solvent-Based, High-Solids
COATINGS ARE USED FOR...

- **Aesthetics**
  - Decoration, Camouflage, Markings
  - Texture

- **Substrate Protection**
  - Corrosion Resistance, Wear, Impact

- **Specialty Functions**
  - Optical, Electromagnetic, Insulation (Electrical, Thermal), Absorption (Sound), Conductive
Coating Formulation Ingredients

- Binders
  - Waterborne
  - Solvent based
- Pigments
  - Hiding
  - Color
- Fillers
- Additives

Wet Coating Formulaion
Dry Coating Film

**Dry Film – Pigmented Coat**
- Pigment/Filler
- Binder

**Dry Film – Clear Coat**
- Binder

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**Example I: Mid-Quality Interior Wall Paint**
- Shelf life > 1 year, heat age and freeze-thaw stable
- Selling price, < $20/gal
- Application by home owner Do-It-Yourself (DIY)
  - Brush and roller
- Easy application, quick dry at 70°F
- Application over old paint, minimum surface preparation
- Low solvent, low odor, easy clean-up
Mid-Quality Wall Paint Requirements

- Color and hiding power
- Low gloss
- Scrub resistance and cleanability
- 3-4 years service life
- Easy touch-up, good color match

Example II: Aircraft Topcoat

- Shelf life: > 1 year, heat age and freeze-thaw
- Cost - $100/gal
- Spray application at airframe manufacturer or depot by professional
- Pot life > 4 hrs (at temperatures up to 90°F)
- Dry time at temperatures from 50 to 90°F:
  - Dry to remove tape: < 4 hrs
  - Dry hard: < 6 hrs
- Application over epoxy primer
Formulating Strategy

I. Define Requirements During Coatings’ Life Cycle

- Raw Materials
- Mixing and Blending
- Storage
- Application
- Drying / Curing
- Shipping / Installation
- Product Life
- Disposal

Interior Flat Wall Paint Formulation

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Pounds</th>
<th>Gallons</th>
<th>NVM-Lbs</th>
<th>NVM-Gals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GRID</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0% Cellulosic Thickener Solution</td>
<td>50.0</td>
<td>6.00</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>120.0</td>
<td>14.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersant, 35% T.S.</td>
<td>8.0</td>
<td>0.81</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Surfactant</td>
<td>2.6</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buffer</td>
<td>2.0</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deviscerant</td>
<td>2.0</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preservative</td>
<td>1.0</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2, Flat Grade</td>
<td>125.0</td>
<td>3.91</td>
<td>125.0</td>
<td>3.91</td>
</tr>
<tr>
<td>Calcined Clay</td>
<td>175.0</td>
<td>9.55</td>
<td>175.0</td>
<td>9.55</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>175.0</td>
<td>7.75</td>
<td>175.0</td>
<td>7.75</td>
</tr>
<tr>
<td><strong>SUB-TOTAL</strong></td>
<td>660.6</td>
<td>43.38</td>
<td>475.0</td>
<td>21.20</td>
</tr>
<tr>
<td>Grind to 4+ H.S.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LET-DOWN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0% Cellulosic Thickener Solution</td>
<td>200.0</td>
<td>24.01</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.0</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LATEX ADD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Vinyl Acrylic Polymer (55.0%)</td>
<td>201.0</td>
<td>22.21</td>
<td>110.6</td>
<td>11.42</td>
</tr>
<tr>
<td>Deviscerant</td>
<td>2.0</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>26.0</td>
<td>3.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Texanol</td>
<td>8.0</td>
<td>1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>51.0</td>
<td>6.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>1148.6</td>
<td>106.03</td>
<td>585.6</td>
<td>32.62</td>
</tr>
</tbody>
</table>

**PHYSICAL PROPERTIES**

Wt./Gal.: 11.5
% Solids, By Weight: 51.0
% Solids, By Volume: 32.6
% PVC: 65.0
% PVC, TiO2: 12.0
% Disp. Solids On pigment: 0.6
% C.S. on Latex NVM: 7.2
## Aircraft Topcoat Formulation

<table>
<thead>
<tr>
<th>Material</th>
<th>Pounds</th>
<th>Gallons</th>
<th>NVM-lbs</th>
<th>NVM-Gals</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Component A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyester polyol (64% solids)</td>
<td>238.0</td>
<td>29.9</td>
<td>200.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>549.4</td>
<td>17.0</td>
<td>549.4</td>
<td>17.0</td>
</tr>
<tr>
<td>DBTD catalyst (1% in MEK)</td>
<td>10.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Surfactant (1% in MEK)</td>
<td>10.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>MEK</td>
<td>177.4</td>
<td>26.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(Component B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isocyanate (75% solids)</td>
<td>233.0</td>
<td>24.0</td>
<td>174.8</td>
<td>18.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1217.8</td>
<td>100.0</td>
<td>926.2</td>
<td>85.2</td>
</tr>
</tbody>
</table>

- % solids, weight: 76.1
- % solids, volume: 85.2
- % PVC: 20.0
- VOC, lbs/gal: 2.6
- NCO/OH: 1.1

## Hegman Grind Gauge

<table>
<thead>
<tr>
<th>Hegman Scale</th>
<th>Depth in mils</th>
<th>Equivalent in microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>87.5</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>62.5</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>37.5</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>12.5</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Reading**
- Scraper
- Dispersion
Important Paint Formulation Parameters

- Pigment volume concentration (PVC)
- Critical pigment volume concentration (CPVC)
- Solids content; non-volatile volume (NVV)
- Volatile organic compounds (VOC)
- Cost
- Stoichiometry
- Volume mix ratios (2 component coatings)

Volume solids (Non Volatile Volume - NVV)

%NVV = \frac{\text{Volume of binder} + \text{Volume of pigment}}{\text{Total volume of wet paint}} \times 100
**Pigment Volume Concentration (PVC)**

PVC is the ratio, by volume, of all pigments & Filler in the coating to total non-volatiles.

\[
PVC = \frac{\text{Volume of (Pigment + Filler)}}{\text{Total Volume of Dry Coating}}
\]

**Critical Pigment Volume Concentration (CPVC)**

CPVC = the PVC where there is just sufficient binder to coat pigment surfaces and fill the voids between pigment particles.

At CPVC striking changes are observed in the properties and behavior of paint films.
Critical Pigment Volume Concentration

CPVC

- Pigment
- Binder

\[
PVC = \frac{\text{Pigment Volume}}{(\text{Pigment Volume}) + (\text{Binder Volume})}
\]

Properties that change abruptly at the CPVC

- **Physical Properties**
  - Density
  - Tensile Strength

- **Permeability Properties**
  - Porosity
  - Blistering

- **Durability**
  - Wet Scrub Resistance
  - Staining

- **Optical Properties**
  - Light scattering
  - Hiding power efficiency
  - Gloss / Sheen

- **Others Properties**
  - Electrical conductivity
  - Block resistance
Pigment Volume Effects on Dried Paint

CPVC

CPVC Depends on the Packing Efficiency
Pigments within Binder

Factors That Effect Packing Efficiency
1. Particle Size Distribution
2. Particle Shape or Shape Distribution
Factors Determining CPVC
Particle Packing

High PVC

Low PVC

Factors Determining CPVC
Particle Size - First Approximation

Q - Which packs more densely - large or small circles?

A - Void fraction the same in each case
Factors Determining CPVC
Particle Size - Other Considerations

Particle

minimum layer of binder

Coated particle is 70% binder
Coated particle is 30% binder

Also: Small particles pack less densely

Factors Determining CPVC
Particle Dispersion - TiO₂ in Mineral Oil

Asbeck, JCT 49, 635, 59 (1977)
Factors Determining CPVC Particle Porosity

Diatomaceous Earth
an empty sphere
CPVC = 0.18

Fumed Silica
very open structure
CPVC = 0.23

Oil Absorption (OA) Value

- Grams linseed oil required to form a paste from 100 gram pigment.
- Oil first coats surface and fills voids; excess needed to turn moist solid into liquid.
- Depends on:
  - Surface area / Particle size (like CPVC)
  - Packing - presence of voids / porosity (like CPVC)
  - Wettability
Significance of OA

- Rough guide to surface area (dispersant demand, adsorption of other materials from liquid paint).
- Also, OA is related to CPVC ...

OA / CPVC Relationship:

\[ cpvc = \frac{1}{1 + (\frac{[OA] \cdot \rho}{93.5})} \]

% void fraction:
- OA if oil
- CPVC if resin
### Particle Shape

<table>
<thead>
<tr>
<th>Material</th>
<th>Size, μm</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium dioxide</td>
<td>0.2 - 0.5</td>
<td>block</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ground</td>
<td>0.6 - 20</td>
<td>block</td>
</tr>
<tr>
<td>Precipitate</td>
<td>0.1 - 2</td>
<td>block, aggregates</td>
</tr>
<tr>
<td>Clays</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ground</td>
<td>0.1 - 5</td>
<td>plate</td>
</tr>
<tr>
<td>Calined</td>
<td>0.8 - 2</td>
<td>plate</td>
</tr>
<tr>
<td>Silica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diatomaceous</td>
<td>4 - 10</td>
<td>irregular</td>
</tr>
<tr>
<td>Talc</td>
<td>1 - 10</td>
<td>plate and fiber</td>
</tr>
<tr>
<td>Mica</td>
<td>8 - 50</td>
<td>flake</td>
</tr>
</tbody>
</table>

### Coating Life Cycle

- Raw Materials
- Mixing and Blending
- Storage
- Application
- Drying / Curing
- Shipping / Installation
- Product Life
- Disposal
Mixing and Blending

- Ease of addition
- Order of Addition
- Ease of Mixing
- Heat build-up
- Foaming
- Shocking
- Health & Safety
- Odor
- Delivery to Storage / Use Tank
- Clean up

Storage

- Freeze-Thaw Stability
- Heat Stability
- Settling of components
- Phase Separation
- Gel-Formation
- Spoilage
Application

- Professional painter vs home owner
- Application Environment
  - Controlled (OEM) vs or On-site
  - Interior vs Exterior
- Method of application
  - roller, slide, slot, blade, curtain
  - brush, spray, etc.
- Delivery to Applicator
- Required film thickness
- Substrate
  - Cleanliness, texture, porosity
- Waste and Recyclability
- Environmental regulations

Drying/Curing

- Drying Conditions
  - Controlled (OEM) vs or On-site
  - Interior vs Exterior
- Sag and Leveling
- Substrate Constraints
  - Temperature Limits
  - Warp
- Defects
- Adhesion
- Environmental regulations
Product Life

- Appearance
  - Color, gloss, opacity
- Mechanical Properties
  - Hardness, flexibility, scrub resistance
- Substrate Protection
  - Corrosion, wear
- Chemical Resistance
  - Stain, acid, base
- Emissions
  - Indoor air quality
- Touch-up and Refinish

Coating Industry

Total Value - $70.6 billion

Global Coating Market – Yr 2000
Current – Approx. $80 billion
Coating Market Segments - US

- OEM Product Coatings
  - Automotive
  - Marine
  - Aircraft
  - Metal Containers
  - Appliances
  - Machinery and Equipment
  - Wood Furniture
  - Plastics
  - Coil
  - Overprint

- Architectural Paints
  - Interior
  - Exterior

- Special Purpose
  - Industrial Maintenance
  - Traffic Paint
  - Auto Refinish

- Miscellaneous
  - Roof, Tank, Deck
  - Concrete

Penetration of Waterborne Coatings – US

<table>
<thead>
<tr>
<th></th>
<th>% Penetration (1985)</th>
<th>% Penetration (2000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OEM Product Coatings</td>
<td>13</td>
<td>26</td>
</tr>
<tr>
<td>Architectural Paints</td>
<td>73</td>
<td>80</td>
</tr>
<tr>
<td>Special Purpose Coatings</td>
<td>7</td>
<td>41</td>
</tr>
</tbody>
</table>
Resin/Binder Producers
Solvent Producers
Pigment Producers
Additive Producers

Specialty Intermediates

Distributors and Resellers

Inspectors

Equipment
Formulators

Contractors Applicators
Distributors and Resellers

Spcifiers/End-Users