Tape Casting and Pre-Formulated Water Based Binder Solutions

Presented by:

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Introduction and Background

- Background in Chemistry and polymers
  - University of Akron and graduate work CMU
- Polymer R&D at Dow Chemical 5 years
- CP Film formulation at Beckman 3 years
- R&D Manager Ferro: solvent binders, electrodes and terminations 10 years
- Polymer Innovations (PII) consulting, custom pastes and water based binder development 5 years
- PII introduces fully formulated WB type water based binder solutions and additives.

Desirable Tape Properties

- Green porosity designed for process
- Ceramic well dispersed
- Strength adequate for processing
- Clean binder burnout
- Lamination and tack designed for process
- No pinholes and uniform thickness

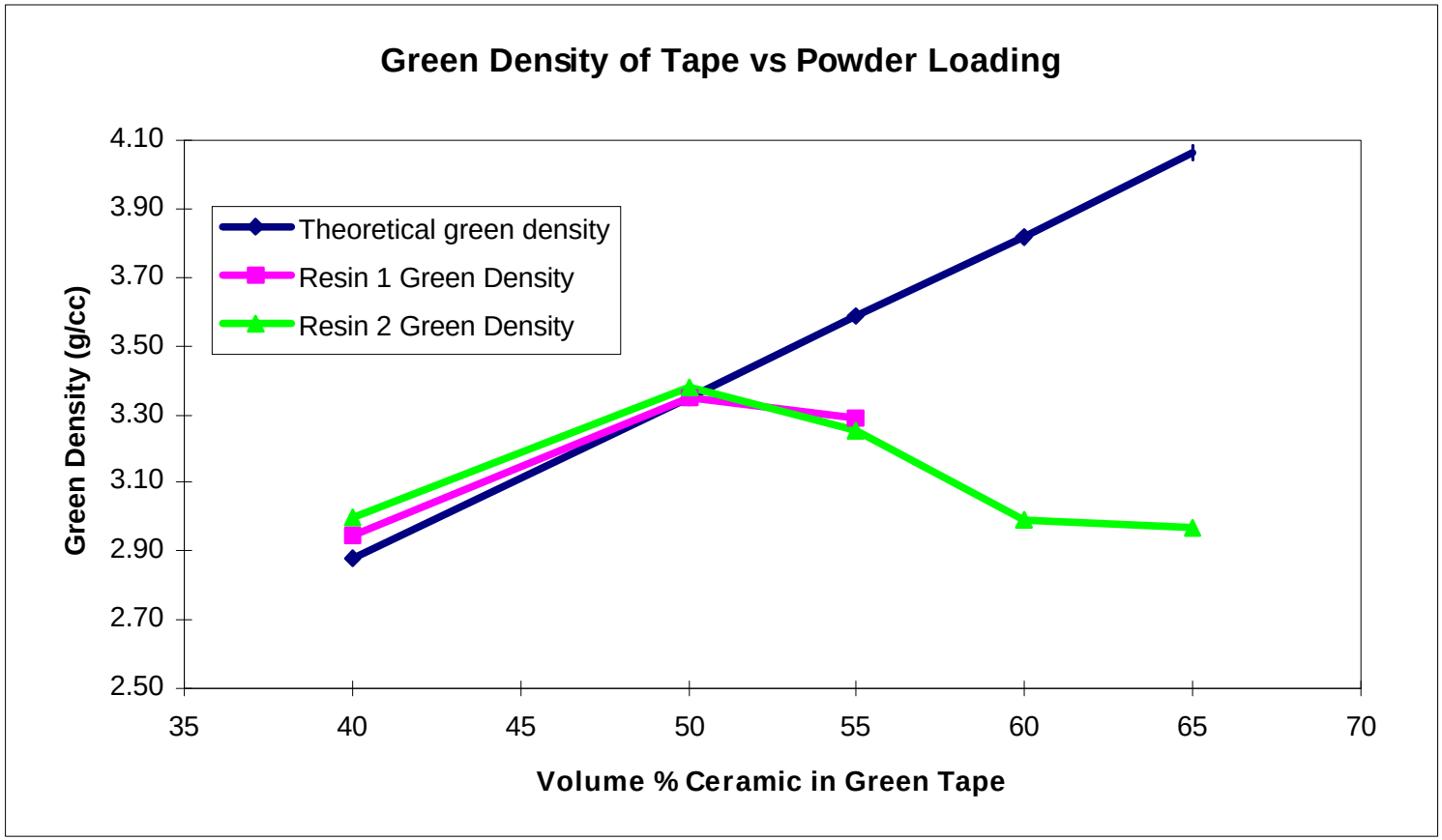
Key Tape Formulation Variables

- Organic solids content of the tape
- Volume % is most universal parameter
  - Determines green porosity
  - Shrinkage during lamination and firing
  - Key in strength and lamination characteristics
- Organic phase formulation (polymer/adds)
- Ceramic Dispersion
  - Agglomerates, voids, and uniformity

Function of Organic Components

- Majority of organics are one phase
- Polymer provides base starting strength
- Plasticizer improves flexibility and lamination
  - Basically is nonvolatile solvent- lowers Tg
  - Increases elongation at cost of tensile
- Dispersant helps deagglomerate ceramic
- Wetting agent lowers surface tension

Pigment Loading Curve



Solvent Based Binder Systems

- Thermoplastic polymer dissolved in solvent
  - PVB and acrylic are common
- Plasticizer soluble in polymer and solvent
- Dispersant dual nature molecule
  - Phosphate or organic esters and acids common
- Solvents typically have low surface tension
- pH and inorganic solubility not issue

Water Based Binder Systems

- Water soluble polymers analogous to solvent type
  - Most common PVoh (also PEG, PVP, PEOx)
- Latex or dispersions
  - Most common is acrylic
- WB4101 Type pH dependent solution
  - Dual properties
  - Special modified acrylic

Water Vs Solvent Advantages

- Not flammable
- Low toxicity
- Ability to use wet ceramic
- Cheaper and easier shipping
- Hazardous cleaning solvents eliminated

Water Vs Solvent Challenges

- Need to lower surface tension for wetting
- Higher tendency for foam
- pH and ceramic solubility control
- Slower drying
- Ceramic type can have effect on properties

WB Type Vs Water Soluble

- Less sensitive to water and humidity effects
- Not prone to boron and other ion gelation
- Balance of ceramic slurry loading/strength to viscosity more favorable

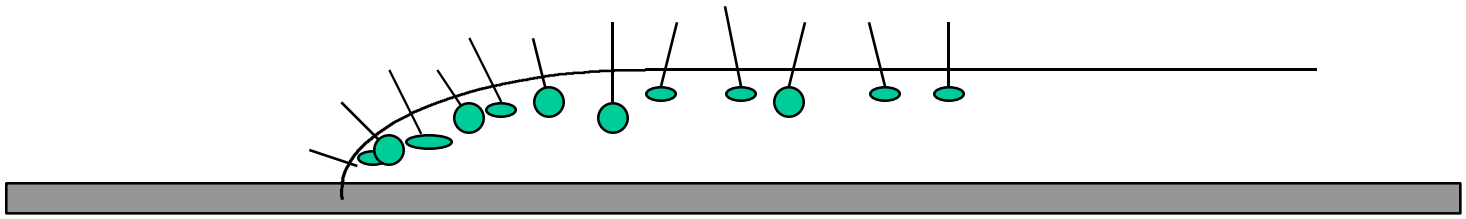
WB Type Vs Latex Type

- More adaptable to solvent process
- Tape characteristics more like solvent type
  - Packing density and lamination
- Polymer and Slip more like solvent
- Tape could in theory be reworked
- Can withstand ceramic milling
- WB type has better wetting to most substrates
- WB type is freeze stable

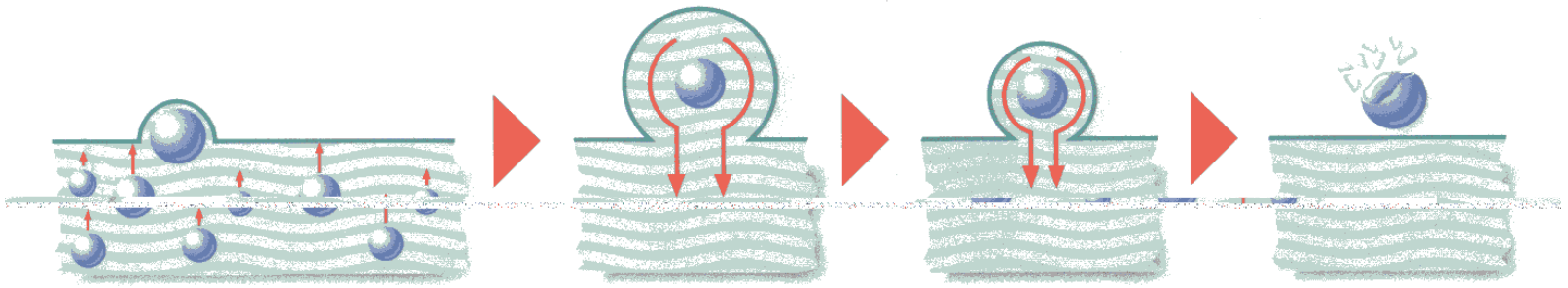
Water Based Wetting

- Water has high surface tension compared to solvents
- Lower surface tension liquid wets higher surface tension surfaces
- Wetting agent has low surface tension half of molecule and polar hydrophilic half.
- Molecules align with low surface energy tails to surface and polar ends to center
- Wetting agent aligns at surface and interface

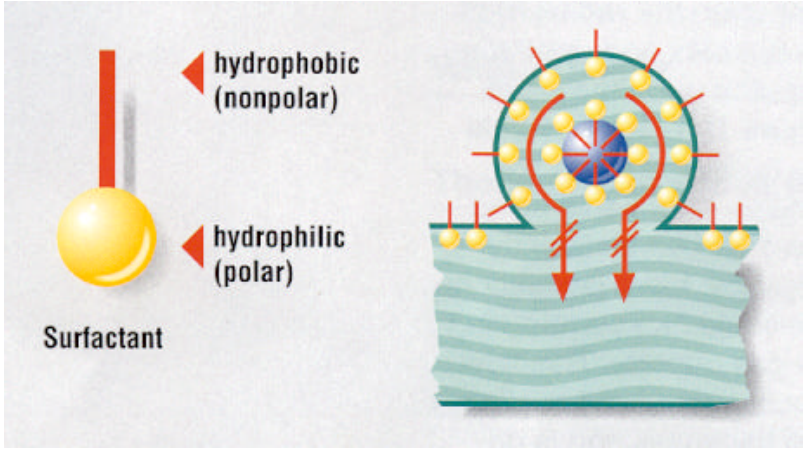
Low Energy Surface Wetting



Foam

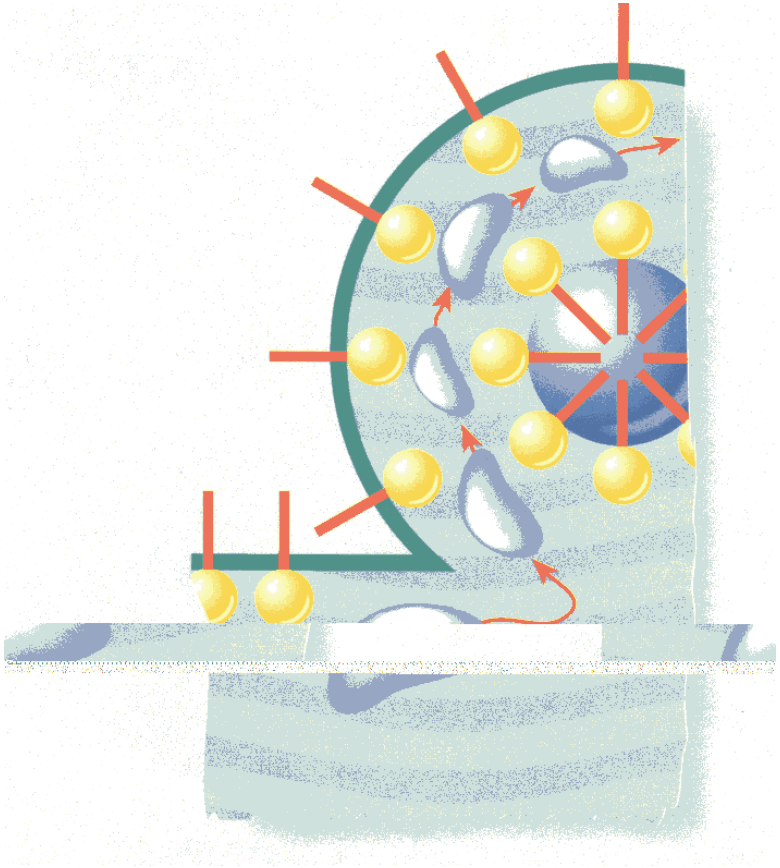

Gas bubbles rise to the surface
The liquid in the lamella flows down and then out.
The lamella then becomes thinner …
… and breaks upon reaching a thickness of approximately 10 nm.

Wetting Agents Can Stabilize Foam



- Wetting agents low surface tension tail goes to air interface
- Polar heads repel each other and do not allow further thinning of bubble wall
- Thus foam can be stabilized

Defoamers



- Defoamers work by limited compatibility and low surface tension
- Compatibility solution Vs film
- Balance foam Vs defects

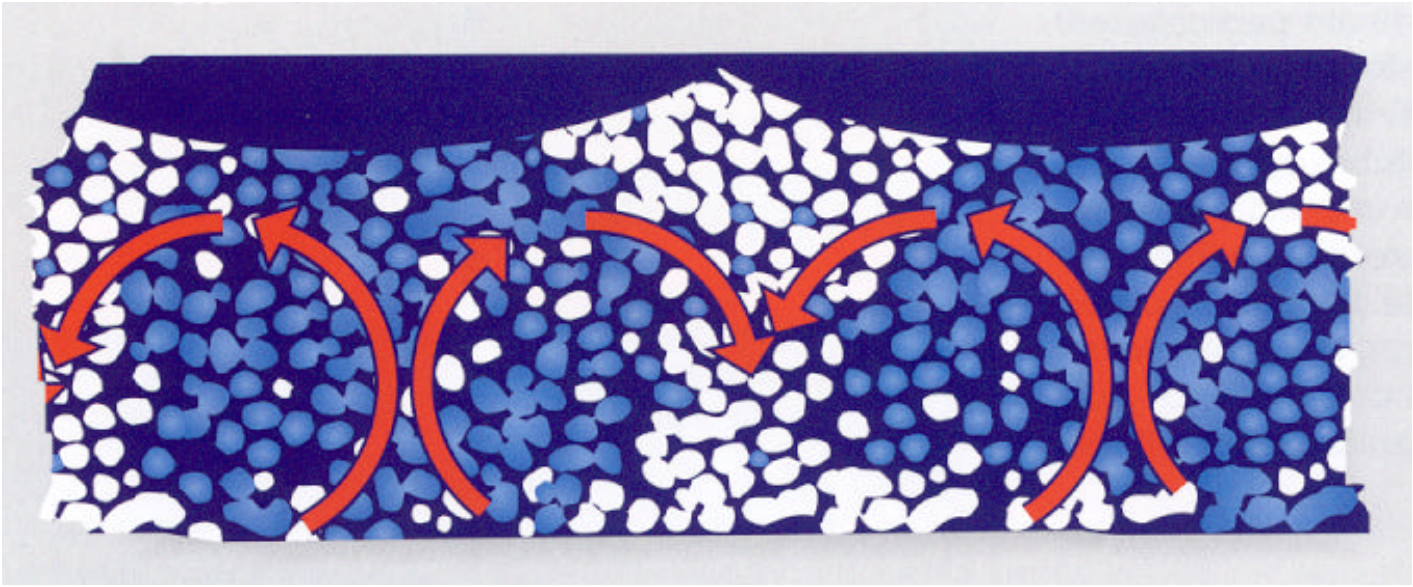
Defoamer Precautions

- Moderation and balance is the key
- High level or strong defoamer eliminates foam
- Surface tension and incompatibility effects
  - Craters or fish eyes
  - Orange peel or flow problems
  - Pinholes (sometimes microscopic)

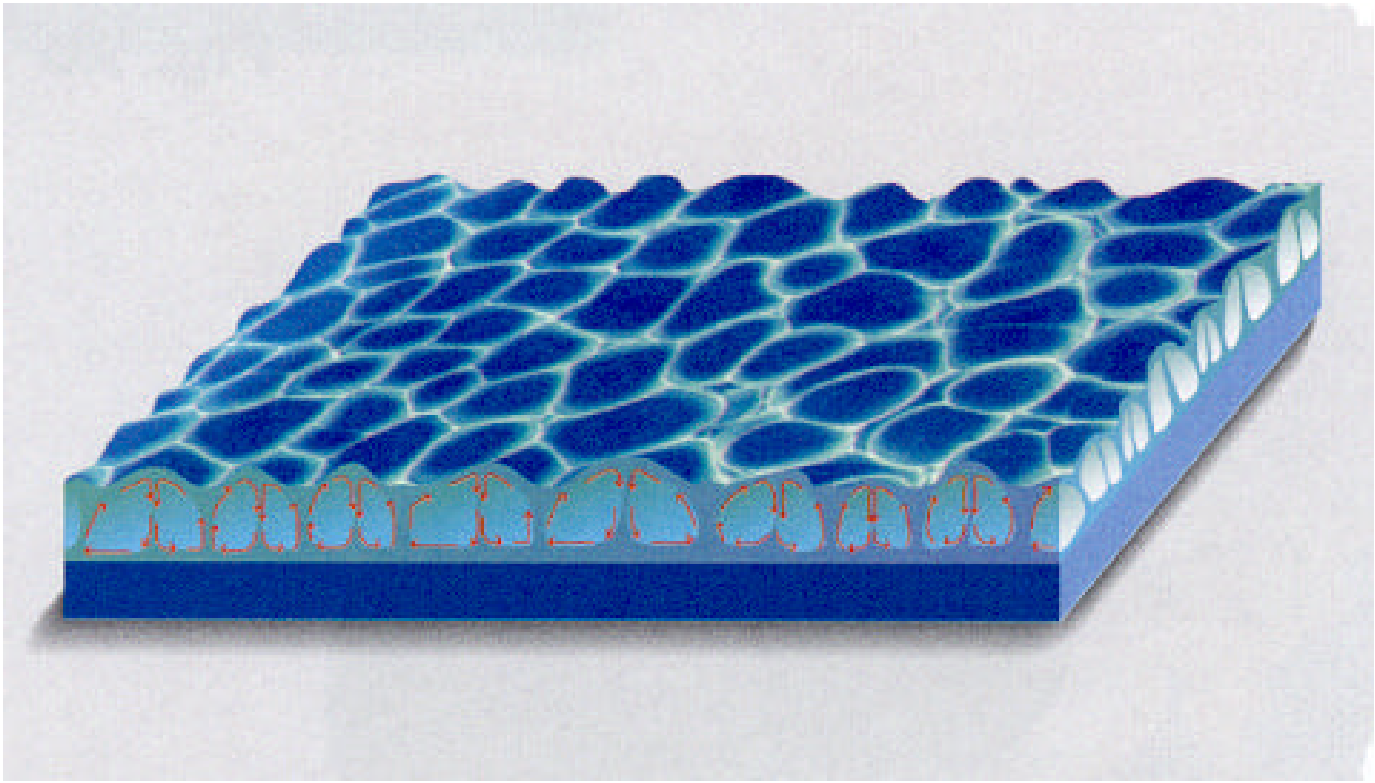
Defoamer/Wetting Agent Balance

- There is not yet any magic defoamer
  - Defoamers rely on controlled incompatibility
  - There must be balance between wetting agent and defoamer
  - Too much defoamer makes defects due to larger second phase of surface active agent
  - Too much wetting agent makes too much foam

Flow Current Defects



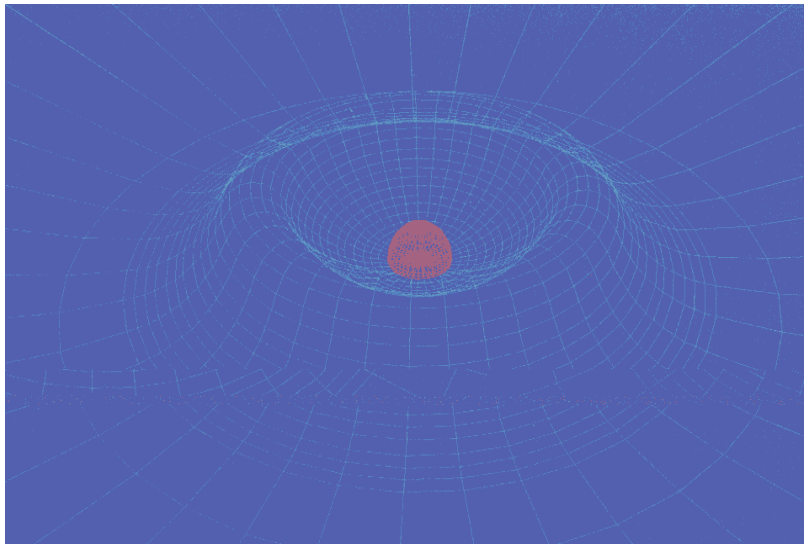
Flow Defects



Mud Cracks and Orange Peel

- Internal flow currents due to:
- Surface tension gradients
  - Excessive defoamer or wetting agent
- Density gradients
- Normal convection effects
- Low viscosity or poor dispersant can worsen

Craters or Fish Eyes



- Low Surface tension second phase.
  - Excess or too incompatible defoamer or wetting agent
- Contaminated particle

WB4101 Components

- Acrylic polymer with functional groups is largest part of the 35% total solids.
- Plasticizer PL001 to adjust flexibility.
- Ammonium hydroxide for pH adjustment
- Wetting agents to provide good cosmetics
- Mild defoamer to minimize foam
- De-ionized Water

Ceramic Differences

- Defoamer balance effected by ceramic
- Effected by other dispersants and other additives
- Strong additive interaction possible due to high surface tension agents.

Available Additives

- PL001: standard plasticizer to increase flexibility and tack.
- WT001: Very mild standard defoamer and assists in wetting powders.
- DF001: Mild defoamer.
- WT002: phosphate ester type dispersant can balance against excess defoamer for crater defects.
- AMP: increase viscosity, pH, plasticity and can reduce casting defects. May increase humidity and heat sensitivity during casting.
- BR002: Allows release of tape from steel belt caster

Milling and Mixing

- WB Type resin is itself a very good ceramic dispersant
  - Therefore at least about 10 - 50% of total binder amount should be in first stage
- WB binder stability is not effected by milling.
- Use of other dispersants typically causes reduction of properties or other problems.

Starting Point Milling

- **<u>Single Stage</u>**
  - 60.0% BT powder
  - 20.0% WB4101
  - 20.0% DI water

- Low shear and lower tape density for given ceramic loading.
- **Contact PII for further technical support.**

- **<u>Two Stage</u>**
  - 60.0% BT powder
  - 5.0% WB4101
  - 20.0% DI water
  - .1%** ammonia hydroxide or amp
- <u>Mill stage 1 add stage 2</u>
  - 14.9 WB4101

- Lower stage 1 viscosity, higher milling energy and tape density.
- More grinding and dispersion.

** for increased dispersant effect

Milling

- Milling can have effect on cosmetics
- Ball Milling
  - 50% of mill volume in media
  - Use normal ball milling speed (60-65% of centrifuging rpm)
- Bead mill: PII has not yet tested for WB4101
- Vibroenergy mill: PII not yet tested maybe better for less foaming

Foam

- Some milling foam is normal
- Slow rolling (less than 5 rpm)
- Let slurry sit for several hours
- Vacuum defoaming
- Care should be exercised during filtering or other processing to not reintroduce foam

pH Effects

- WB Type binders not soluble in low pH (less than pH about 6.5).
- Increasing pH greatly increases binder viscosity.
- Normally no pH adjustments are required.
- Water with some ammonium hydroxide (or window cleaner) cleans dried deposits effectively.

Tape Tests at PII

- Cosmetics
  - Wetting of siPET
  - Craters, orange peel, agglomerates and 45X pinholes
- Green Density (for given ceramic loading)
- Puncture strength and crease test
- Viscosity
- Lamination Behavior
- Adhesion to substrate
- Please contact PII for technical support.