TAPPICON®

Coating: Back to Basics
Coating Materials Review



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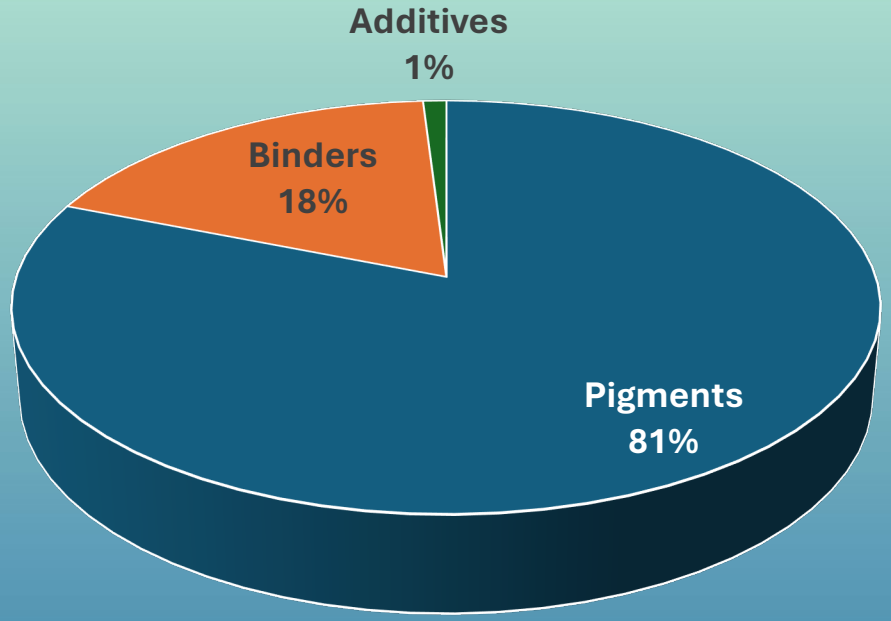
Presentation Outline



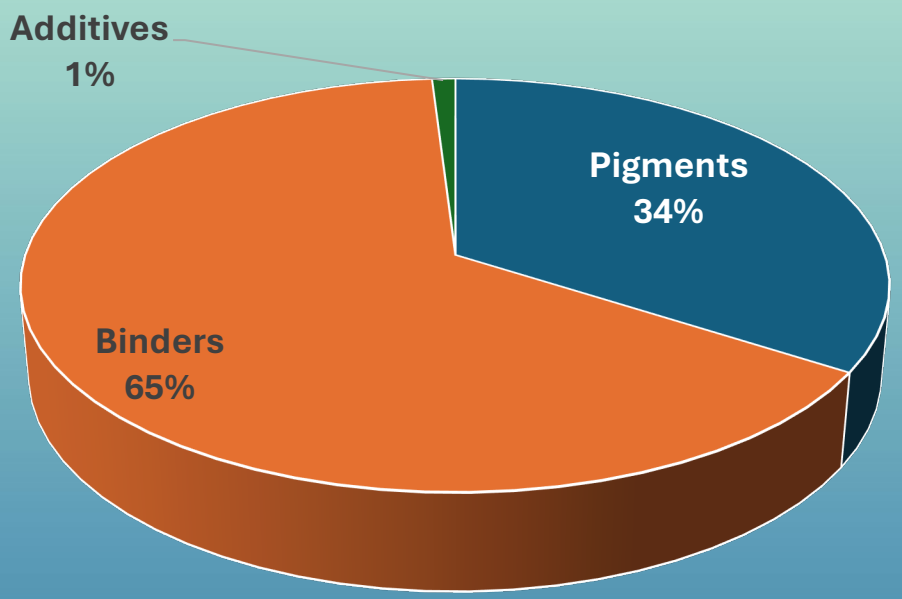
- Pigments
  - Kaolin Clay
  - Calcium Carbonate
  - Synthetic Pigments
  - Titanium Dioxide (TiO_2)
- Binders:
  - Natural Binders: Starch, Protein
  - Synthetic Binders: Latex, PVOH
- Additives
  - Dispersants
  - Foam control
  - Insolubilizers
  - Flow/water retention modifiers
- Formulating for:
  - Printable coatings
  - *Barrier coatings*

Two types of coatings, how do they differ?

Printable Paper/Board Coatings



Barrier Coatings



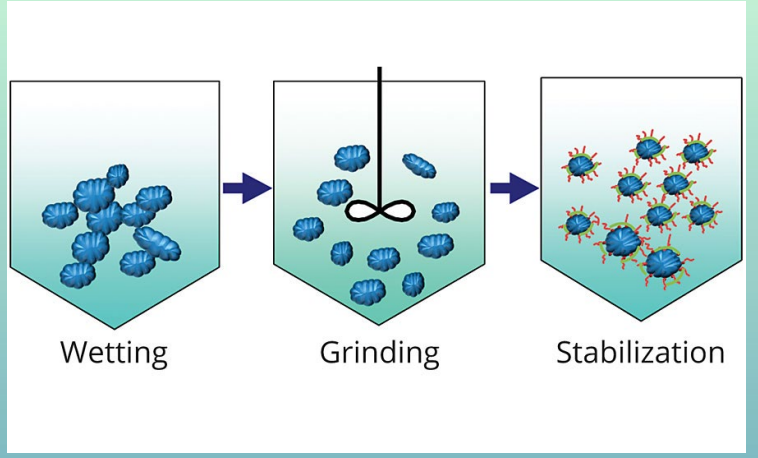
- If you said that the left one is where the paper coating industry was concentrated and the right one is where it's going, you're correct.
- ***Barrier packaging is our future!***
- We'll consider coating materials with respect to both in this module

Paper Coatings: Three broad classes of ingredients

- **Pigments:** presented in collaboration with *Prakash Malla*, Thiele Kaolin, retired
- **Binders:** presented in collaboration with *Meggan Hostetler-Schrock*, Primient
- **Additives:** presented in collaboration with *Gordon Bugg*, Kemira

Pigments, Ideal Properties

- Platy vs. Blocky vs. Structured
- Good coverage effect
- High solids content dispersions
- High brightness
- Cost effective
- High refractive index
- Low binder demand
- ***Enhance barrier coating effectiveness***

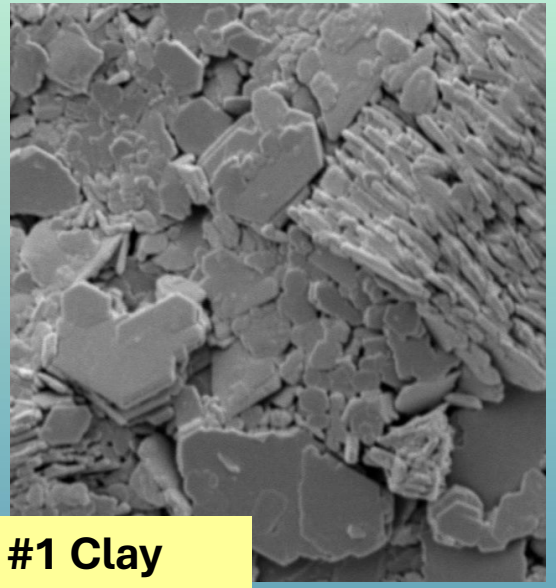




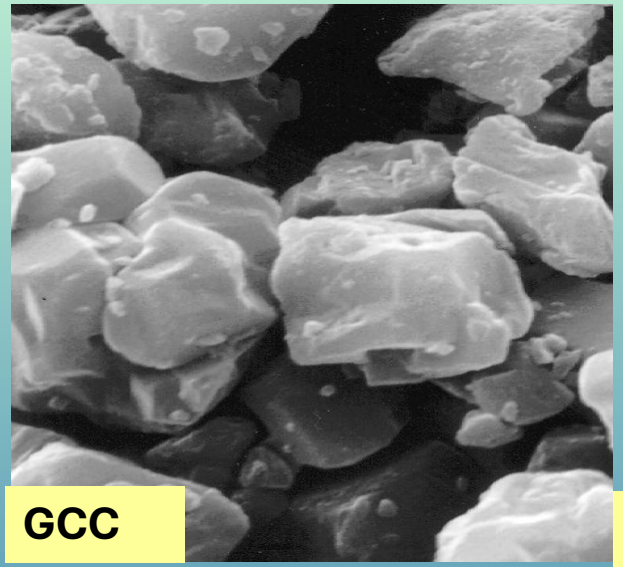




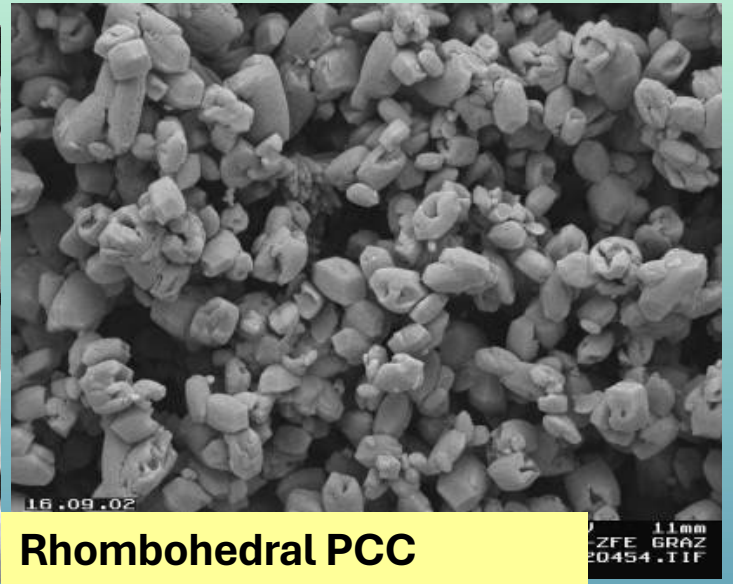
Typical Pigment Morphologies



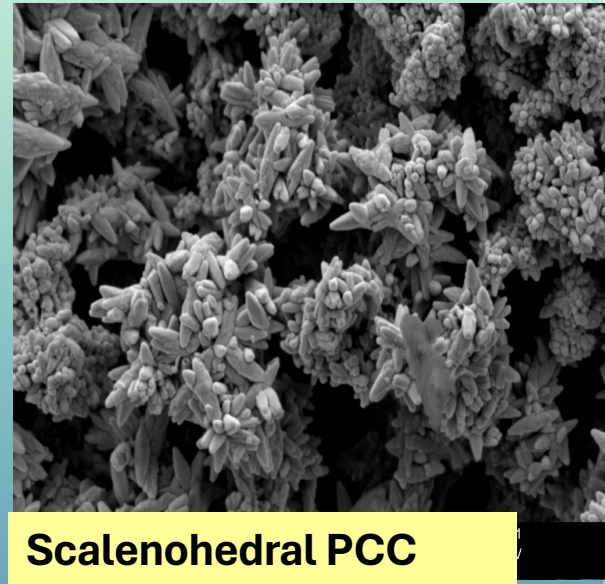
#1 Clay



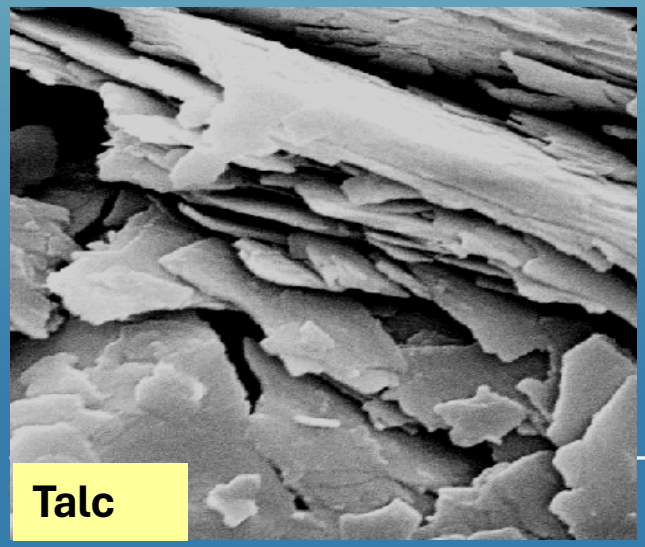
GCC



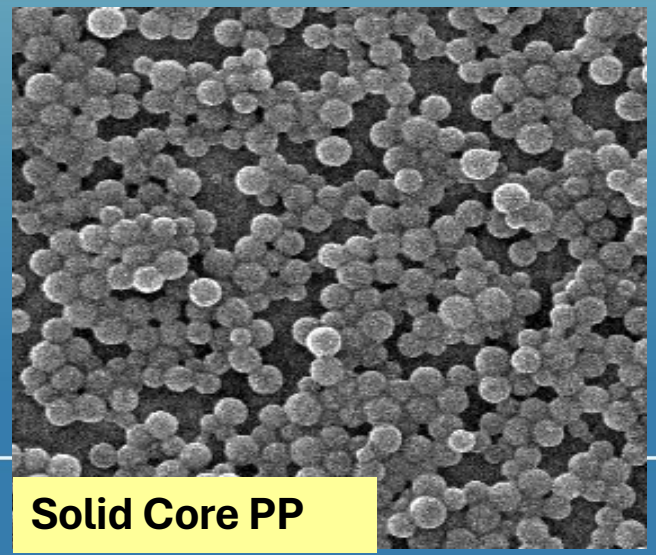
Rhombohedral PCC



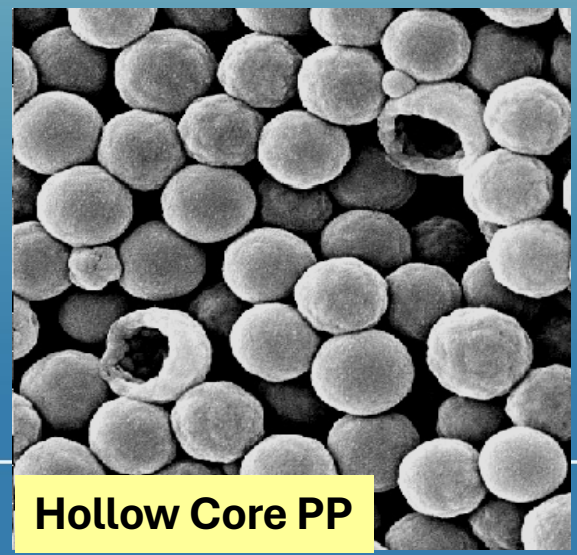
Scalenohedral PCC



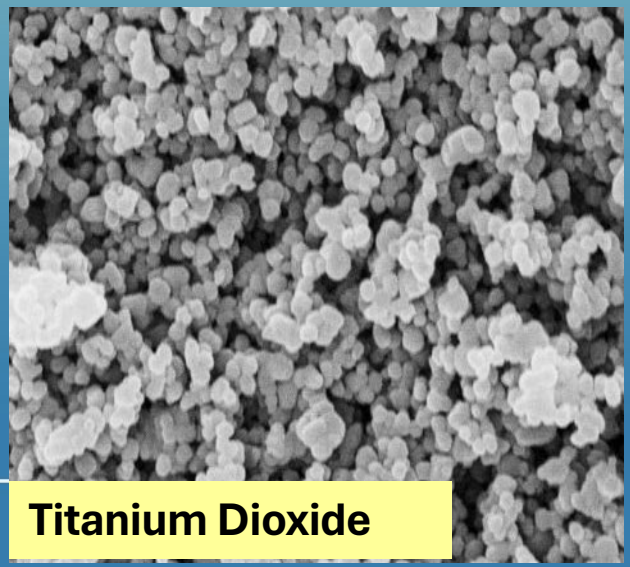
Talc



Solid Core PP



Hollow Core PP



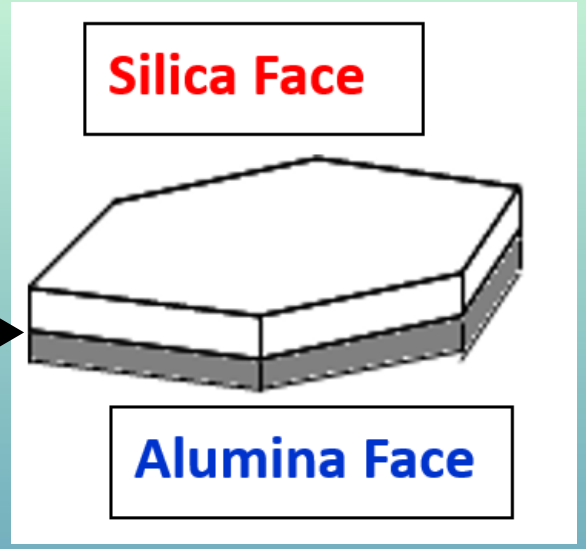
Titanium Dioxide

Pigment Types

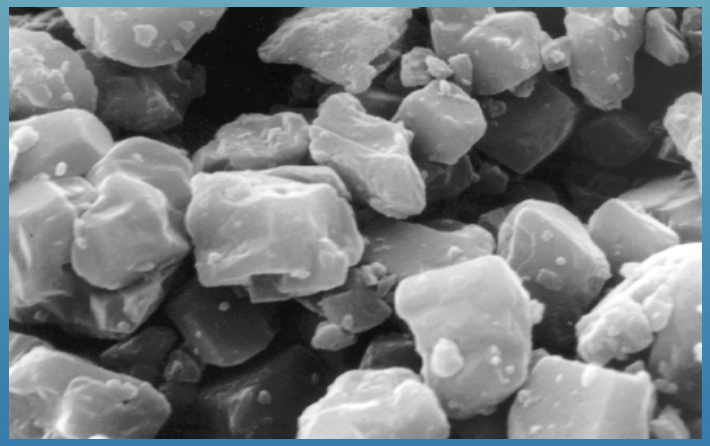
- Ground Calcium Carbonate ($CaCO_3$)
- Kaolin Clay
- Calcined Clay
- Titanium Dioxide (TiO_2)
- Synthetic Latex Pigments (“Plastic Pigment”)
- ***Highly Platy Pigments for barrier coatings***

Clay vs. Carbonate: Advantages and Disadvantages

- **Clay:**
  - Platy morphology, low coat weight fiber coverage, anisotropy between faces, ***barrier coating enhancement***
  - Lower slurry solids, moderate brightness, ***poorer folded barrier properties***, lesser coating runnability

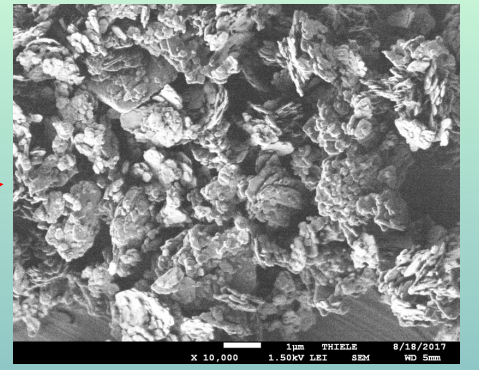


- **Calcium Carbonate (GCC/PCC):**
  - Blocky morphology, high brightness, high solids, excellent coater runnability, ***good folded barrier properties***
  - Better in high coat weight systems, generally poor hiding power, ***less contribution to barrier properties.***



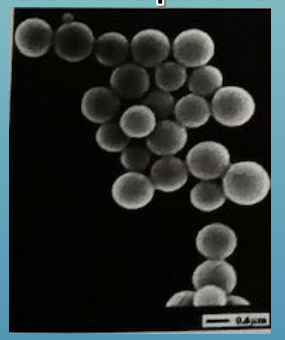
Other Pigment Advantages and Disadvantages

- **TiO_2:**
  - High brightness and exceptional opacity/hiding power
  - Cost and availability
- **Calcined clay:**
  - Highly structured morphology, high brightness, excellent low-cost opacity/hiding power (TiO_2 replacement)
  - Poor rheology limits its use in high-speed coating operations.
- **"Plastic pigment:"**
  - High glossing, opacity/hiding power for hollow sphere
  - Cost, achieving high solids more difficult
- **Highly platy:**
  - Good surface coverage, ***contribute highly to barrier coating effectiveness***
  - Difficult rheology for high-speed coaters, cost

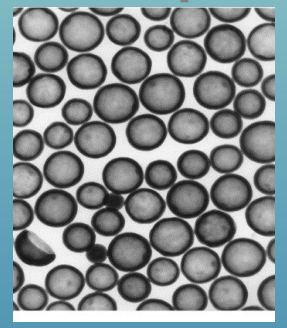


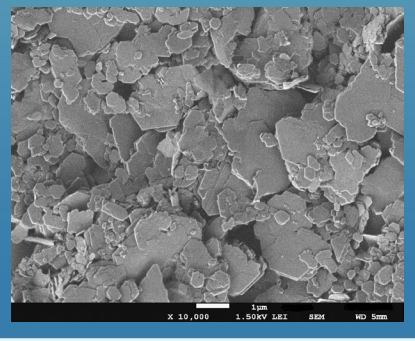
Calcined Clay

Solid Sphere



Hollow Sphere





Coating Binders

- Provide the cohesion that binds the coating pigment particles together and adhesion of the coating layer to the basesheet
- Provide strength required for coated paper to pass through printing and converting operations and for board glueability
- ***Impart water resistance to the coated surface***
- They are key in determining
  - The flow and leveling properties of the applied coating
  - The printability of the coated paper

Binder Requirements

- Strength
  - Good pigment bonding strength
  - ***Rapid, strong film-forming for barrier coatings***
- Compatibility
  - with pigments
  - with other binders
- Viscosity / Rheology / Stability
  - in coating formulation
    - water holding
    - Low and high shear viscosity control
- Performance
  - good color
  - glossing
  - ink / varnish holdout
- Low Cost / Good Availability

Two Classes of Binders

- Natural Binders
  - **Starches**
    - **Corn, wheat, potato**
    - **Tapioca and rice**
    - **Can be converted and modified to affect properties**
      - **Enzyme, AP converted**
      - **Ethylated, oxidized**
  - **Soy Protein**
    - **Converted in alkali media**
    - **Limited use in paper coatings in recent years**
- Synthetic Binders
  - **Latexes**
    - **Many different types - SB, SBA, SA, Acrylic, Acetate/Acrylic, PVAc**
  - **PVOH/EVOH**

Relative binding strength

Material	Parts for Equal Strength
PVOH	1
Starch	3.0 - 4.0
Soy Protein	2.5 - 3.0
SB Latex	1.5 - 2.0
Acrylic Latex	2.0-2.5
PVAc/Acrylic Latex	2.5 - 3.0

Starch Binders

Formatting courtesy of:

Meggan Hostetler-Schrock

Primient

Features of Natural Binders

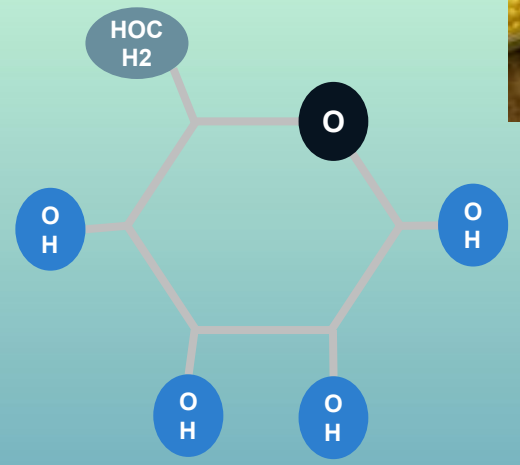
- **Natural binders**
  - **Cost, rheology, water retention,**
  - ***Effective biodegradable oil/grease barrier***
  - **Easily modified for expanded properties range**
  - **High viscosity, low solids**
  - **Subject to bacteriological degradation**
  - **Need to be cooked and or converted**
  - **Variable strength depending on degree of conversion and modification**
  - **Binder movement during application and drying.**

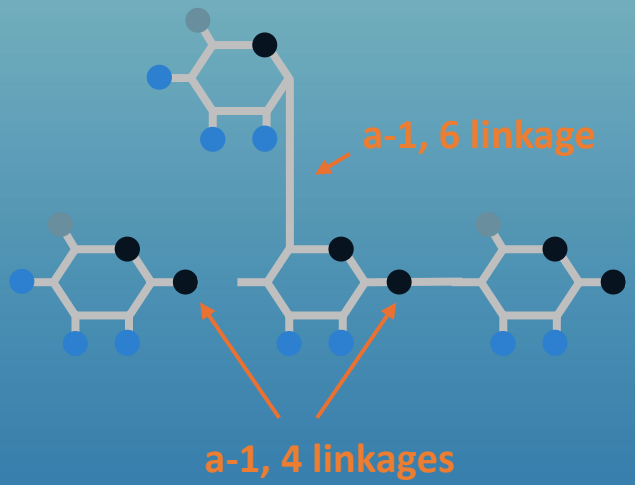
What is Starch?

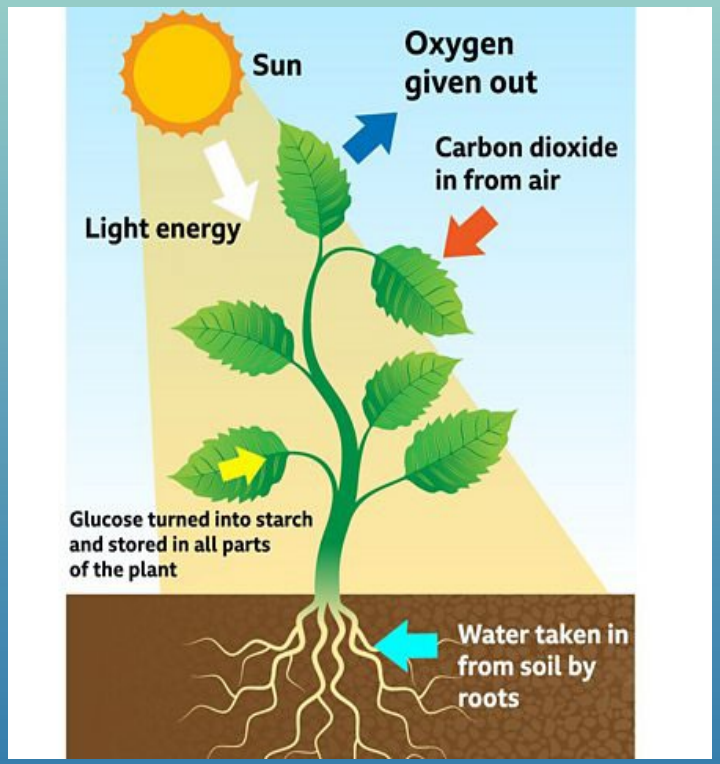


- A white, granular, bio-polymer material produced by all green plants

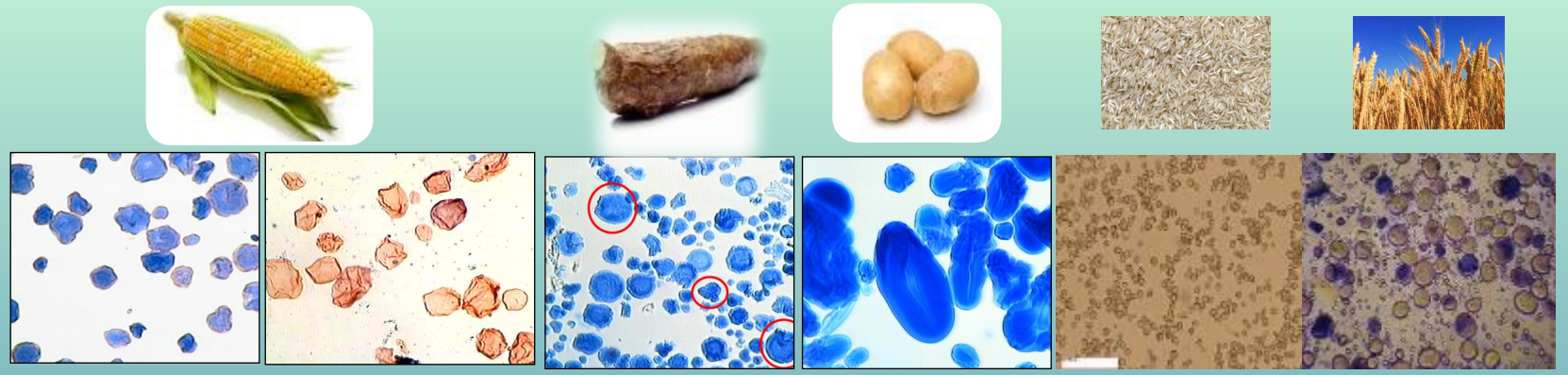
- Polysaccharide comprising glucose monomers – sugar building blocks
- Two fractions:
  - Amylose
    - straight chain
    - 250 - 2000 glucose units
  - Amylopectin
    - branched
    - millions of glucose units







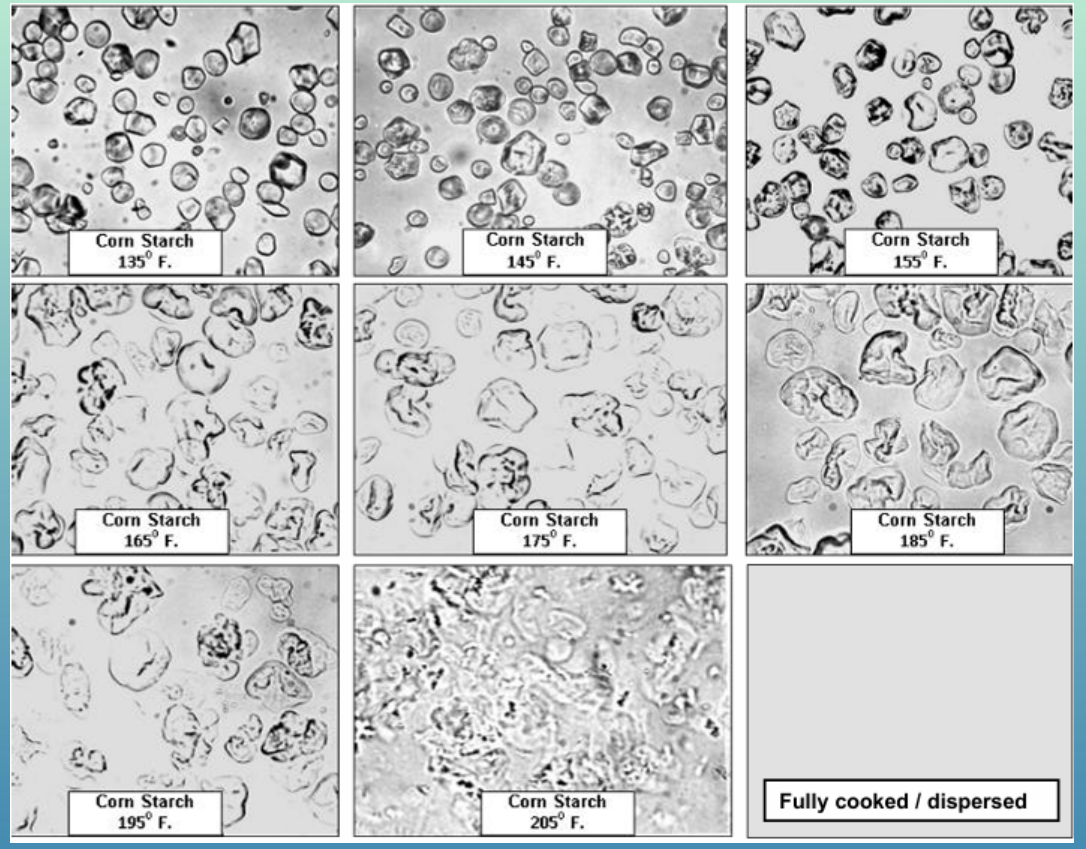
Sources and Properties of Native Starch



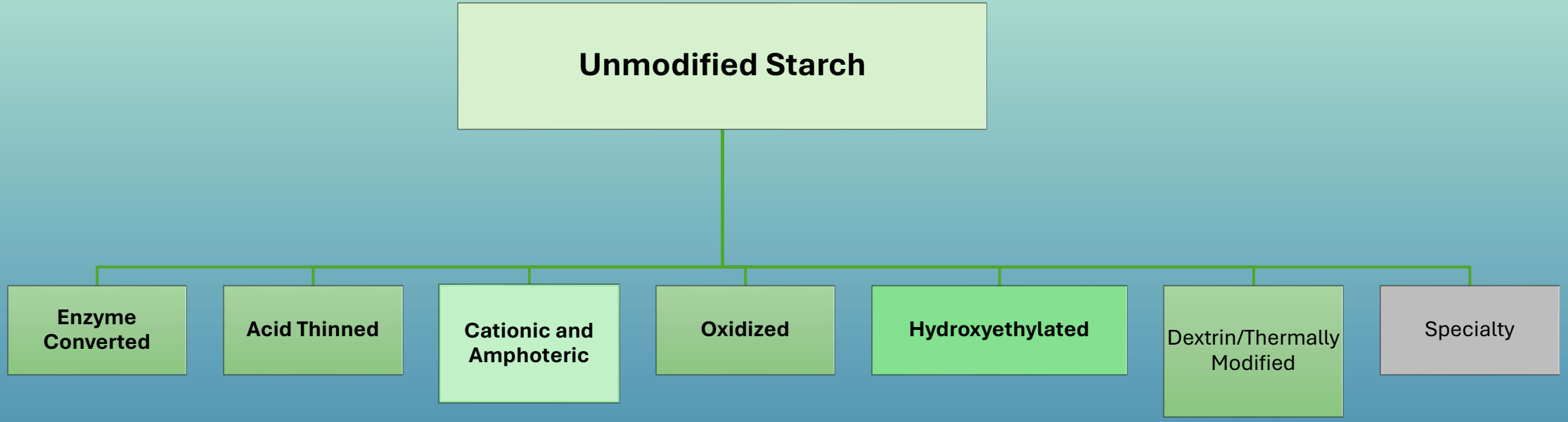
	Maize	Waxy Maize	Tapioca	Potato	Rice	Wheat
Amylopectin / amylose[1]	72% / 28%	99% / 1%	80% / 20%	75% / 25%	74% / 26%	74% / 26%
Shape	Polygonal or Angular Rounded	Polygonal or Angular Rounded	Rounded Bell-shaped	Oval, Egg-shaped	Polygonal	Flat, Elliptical, Rounded
Granule size (long axis; µm)[2]	5-25	5-25	5-35	15-100	3-8	<10 & 20-35
Gel Formation	Firm	Non-Gelling	Soft	Salve	Firm	Firm

Elements of starch binder

- Cost
  - relatively low compared to latex
  - shipped to mill site as a solid (10% moisture)
- Performance
  - good water holding
  - viscosity control in coating color
  - reasonable film strength
- ***Biodegradable***
  - ***Compostable barrier packaging***
- Must be “cooked” for binder use (temperature profile)



Starch Chemistry – Modifications



Typical formulations

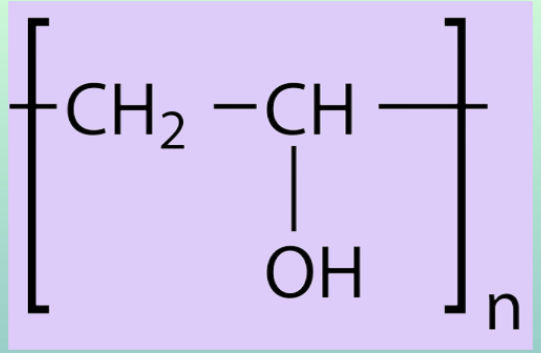
- LWC grades
  - Low solids formulations (> 50%) use higher starch levels (10-12 parts) to increase viscosity
  - MWC may use lower levels (6-8 parts) to compensate for higher solids in coating
- CFS grades
  - Tend to use lower levels (2-4 parts) for print quality, brightness, color and gloss

- ***Barrier Coatings:***
  - ***Starch film application for OGR.***
  - ***Widely used in Quick Service Restaurant compostable packaging***
  - ***Crosslinking may help a bit with water resistance.***
  - ***Many products in this space are specialty starches***

Features of Synthetic Binders

- **Synthetic binders**
  - **Low viscosity high solids,50%**
  - **Mechanically, chemically and biologically stable**
  - **Stronger than natural binders**
  - **Thermoplastic for strength and easy gloss development**
  - ***Good combination of oil/grease & water resistance in barrier coatings***
  - **Can be modified for specific properties**
    - **Particle size**
    - **T_g: monomer blend**

Polyvinyl Alcohol/EVOH



- Synthesized by hydrolysis of vinyl acetate homopolymer
- Water soluble:
  - Like starch it's subject to limitations of solution polymers
    - Low solids/high viscosity.
    - Tends to follow water during coating application and drying
    - Poor water resistance
- High binding strength
- Excellent carrier for optical brightening agents (OBAs)
- High cost relative to other coating binders
- ***Used in Oil/grease and Oxygen barrier coating layers***



Latex Overview for Paper Coatings

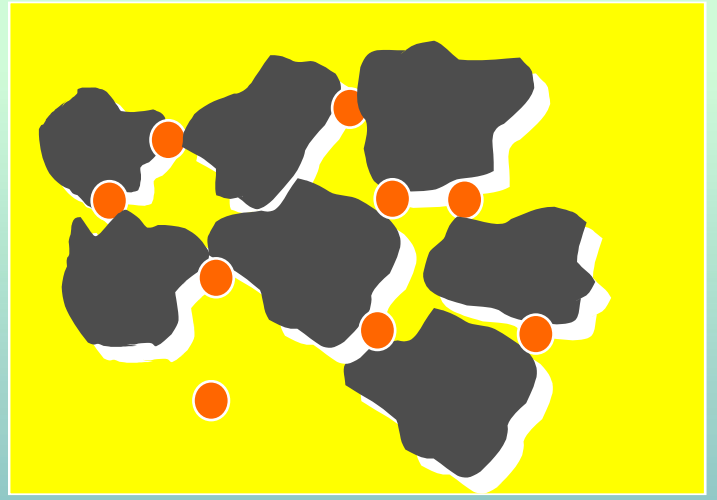
- Typically hard monomer/soft monomer copolymers (Tg)
- Hard monomers: Styrene/MMA (105 T_g), Acrylonitrile (95-130 T_g), Vinyl Acetate (28-45 T_g)
  - Tensile strength and hardness
  - Gloss
  - Stiffness
  - Porosity
  - ***Non-blocking barrier coatings***
- Soft monomers: Butadiene (- 40 T_g), Butyl acrylate (-55 T_g)
  - Binding strength
  - Film formation
  - ***Flexible, non-cracking barrier coatings***

Latex Overview - Properties

- **Glass Transition Temperature (T_g)**
  - **The temperature above which a polymer changes from a hard, glassy state to a soft, rubbery state.**
  - **Higher T_g = firmer latex film**
- **Particle size**
  - **Reported as the weighted average spherical particle diameter, usually 1000 to 2500 angstroms**
    - **100-250 nanometers (nm)**
    - **1,000-2,500 Angstroms (Å)**

Latex Overview – Functional Monomers

- Functional Monomers (Carboxylation, Amides)
- Colloidal stabilizers (PVOH, CMC/HEC, solution acrylics)
- Both of the above:
  - Affect latex stability, interactions
  - Influence paper coating rheology, water holding and strength.
  - ***Also influence barrier coating properties such as film formation and blocking resistance***



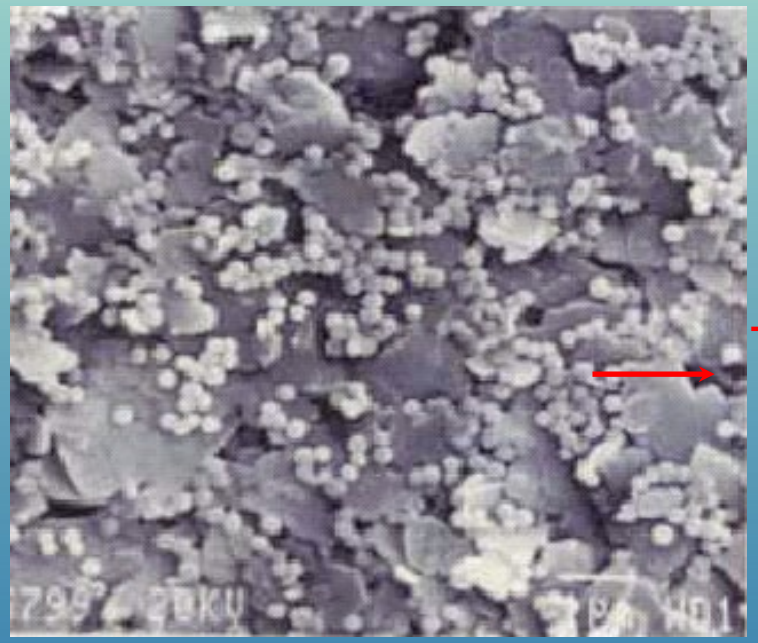
latex particles pigment particles



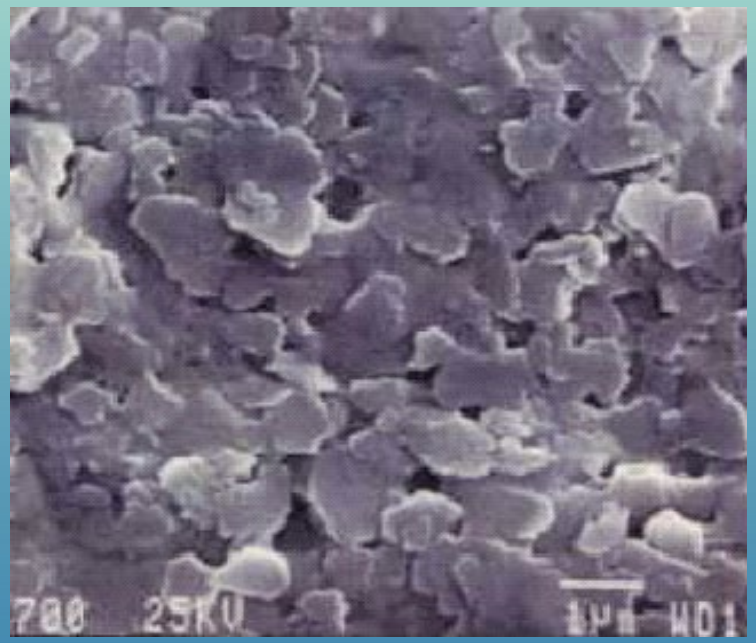
Film Formation

- In order to bind pigments together or form an effective barrier coating, the binder must form a film

Kaolin + 10 pph SBR latex



+ Heat



Wet state

(SEM-analysis of a coating Cryoscopic fixation)

Dry state

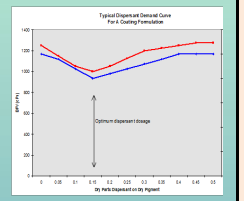
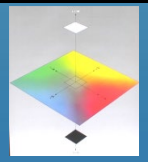
Coating Materials
Additives

Additives (0.1 to 2.0 parts)

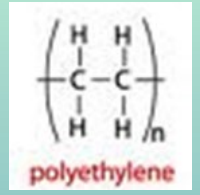
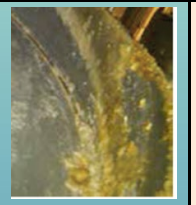
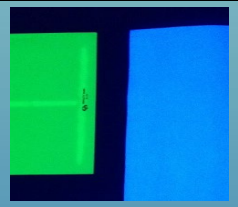
Minor but necessary, materials make the difference between success and failure.

- Dispersants
- Foam control agents
- Insolubilizers/ (Crosslinkers)
- Thickeners/ Rheology Modifiers/ Water Retention Aids
- Lubricants
- Preservatives
- Dyes including OBAs

Additives

Component (Additive)	Function	Comments
Dispersant 	Disperse pigments to reduce flocculation, settling and lower the viscosity for better coating handling and flow	Amount customized for each coating formulation by running a dispersant demand
Rheology Modifier 	Achieves the desired low shear, high shear rheology and coating water retention properties	Added to affect the wet coating properties. May be synthetic (ASE, HASE) or natural (starch, CMC, alginate) origin.
 Defoamers & Anti Foams	Keeps coating from entraining air, reduces foam that has already been generated.	Adversely impacts other coating properties. Many times foam issues can be resolved with a mechanical solution
Insolubilizer/Crosslinker (known by either term)	Render the dried coating resistant to re-wetting and dissolving	Reacts with the binder in the coating. May also impact white pitch deposition, printability
 Dyes & Colorants	Control tint, shade of final coating per customer specification	Major types include pigmented and direct. Applied in wet end and/or in the coating

Additives

Component (Additive)	Function	Comments
 Lubricants	Processing aid for the wet coating, coating application or converting steps	Five chemistries in use. Used to impact CoF, gloss, release properties, cutting & reduce buildup on coater
Biocide/ Preservative 	Control microbiological growth, prevent spoilage	Plate counts and similar means used to evaluate. Usually the smallest additive application (if used)
 Optical Brighteners	Enhance apparent brightness of the coating. May be applied in the coater, wet end or SP	Uniform application critical to avoid mottle. May have problem if TiO2 is also present in the coating
Functional Additives	A general category for very small-use, specialized applications	Includes anti-static, frictionizers, surfactants, barriers
pH control	Adjust final coating pH to target. Typically caustic or aqua ammonia are used	Coating performance is highly influenced by the pH, including print properties (ink lay)

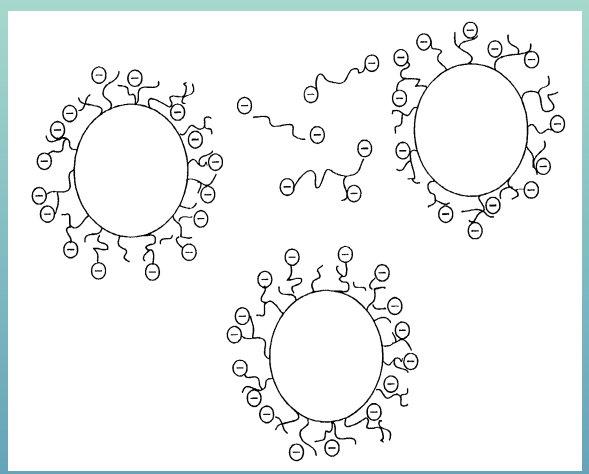
Role of Dispersant

- **Disperses the coating pigment, resulting in:**
  - **Lower viscosity & improved flow that allows for the highest possible coating solids**
  - **Improved stability**
  - **More uniform coating**
  - **Fewer pigment aggregates (clumps) that can cause streaks, scratches, and blade deposits**

- **Dispersing the pigment means overcoming the attraction that the pigment particles have for each other**

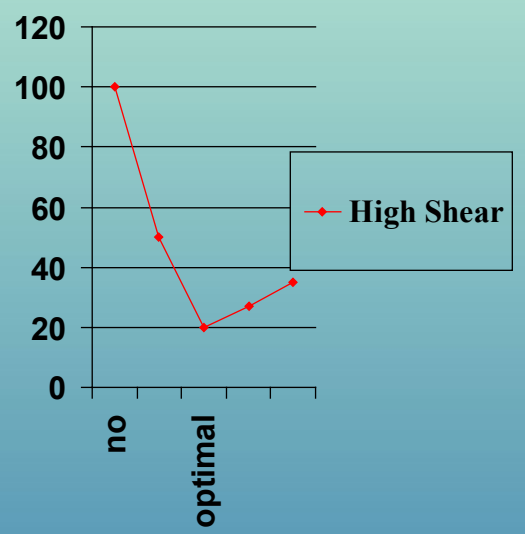
Dispersion Stability

- Dispersant added during pigment manufacture is a source of negative charges
- Surfactant is mobile in the water phase, and is strongly attached to the pigment but may be attracted elsewhere
  - To other pigment particles
  - To other formulation ingredients
- The stability resulting from dispersants can be upset by
  - Excess dilution
  - Chemistry, i.e. incompatible defoamer
  - Microorganisms



Determining Optimal Dispersion

- **Dispersant Demand:** This test demonstrates whether the coating is optimally dispersed. In coatings the viscosity is related to the degree of association of the negatively charged pigment particles.



Role of Coating Defoamer / Deaerator

- **Minimizes entrainment of air in the coating (antifoam)**
- **Removes entrained air from coating (defoamer) reducing**
  - **Coating skips**
  - **Pump cavitation**
  - **Coating density decreases**
- **Prevents or eliminates surface foam**

Note that the terms DEFOAMER, DEAERATOR, and ANTI-FOAM are often used interchangeably today

Sources of Foam in Coating Colors

Source

Coating Kitchen

- Pumps
- Backflow from the coater
- Mixer

Coater

- Applicators
- Splash
- Pumps
- Overflows



Role of Insolubilizers

- Used to crosslink or insolubilize starch, protein, polyvinyl alcohol -- increases water resistance of the coating
- Prevents piling, linting and milking on press
  - Improve wet rub resistance
  - Improve wet/dry strength
  - Increase condensation holdout
- ***Barrier coating crosslinking***
  - ***Reduces blocking tendency***
  - ***Also improves barrier coating abrasion resistance***
  - ***Improves water resistance***

Insolubilizers (Crosslinkers)Types

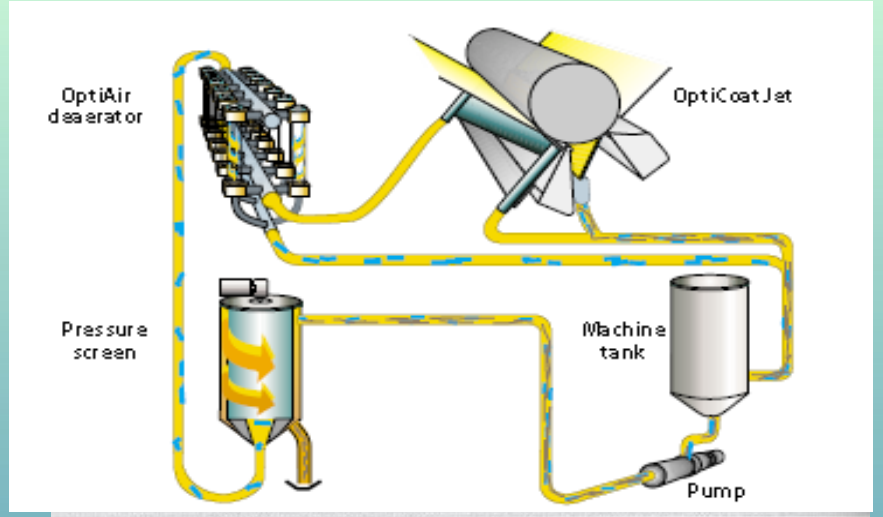
- Amino Resins
  - Melamine Formaldehyde (MF)
  - Urea Formaldehyde (UF)
  - Very limited use due to concerns with formaldehyde.
- Metal Salts (used commonly with carboxylated systems)
  - Zirconium (the dominant metal salt used in insolubilizers)
    - Ammonium Zirconium Carbonate (AZC) (the dominant Zirconium product)
    - Potassium Zirconium Carbonate (KZC)
- Glyoxal (used commonly with starch)
  - Glyoxal-base Resins (Modified or Blocked)
    - Blocking delays crosslinking reaction until drying stage
- Zinc Oxide Complex:
  - ***Excellent for carboxylated latex crosslinking in barrier compounds***
  - Zinc may be a problem for some users

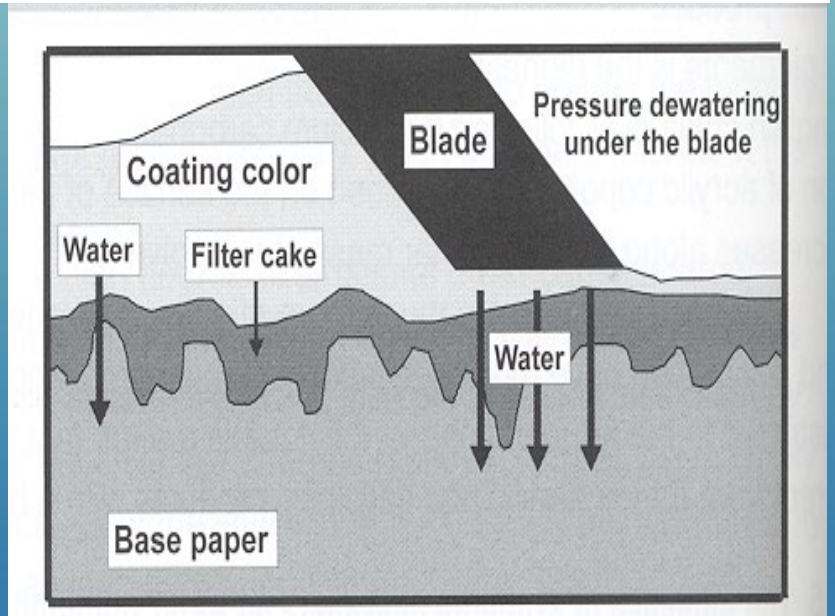
Role of Rheology Modifiers & Thickeners

- **Builds viscosity (Brookfield and /or Hercules)**
- **Improves coater runnability**
- **Improves water retention. Improved water retention can control the following:**
  - **Coating strike-through and migration**
  - **Coater blade streaking and weeping**
  - **Control of solids in coating return**

Rheology Modifiers: Why they are used?

- Affect coating viscosity
  - Low shear for pumping and application
- Need to control flow behavior (rheology) of the coating under variety of conditions:
  - extremely high shear (10^6 sec^{-1})
  - sudden changes in shear forces
  - rough, non-uniform, absorbent surface
  - highly filled coating





The water retention of the coating color influences the thickness of the filter cake together with the absorbency of the base paper.

Types of Rheology Aids

- **Natural Products**
  - **CMC, HEC**
  - **Alginates**
  - **Starch**
- **Synthetic Products**
  - **Alkali-Swellable Emulsions**
  - **Associative Thickeners**
  - **Polyvinyl Alcohol**

Role of Coating Lubricant

- Improve flow at blade
- Reduce whiskering at blade
- Prevent dusting at supercalender
- Improve gloss at supercalender
- Prevent edge cracking in final sheet
- ***Enhances blocking/abrasion resistance in barrier coated papers***

Types of Lubricants

- **Calcium Stearate Based**
  - **Economical**
  - **Widely utilized**
  - **Best performance at dry end**
  - **Low dusting with supercalendering**
  - **Low residue**
- **Soy-Lecithin/Oleic Acid Blends (Diglycerides)**
  - **Lower viscosity build with starch**
  - **Good for Hot/Soft and high temperatures**
- **Wax Emulsions**
  - **Paraffin, Polyethylene**
- **Dispersed Tallow**

Role of Coating Preservative

- **Preservatives prevent spoilage of coating after makedown**
  - **Coatings containing natural products most susceptible**
    - **starches and proteins**
    - **organic dispersants**
    - **natural thickeners**
- **Allows coating storage during short (ca. 8 hour) machine downtimes**
- **Eliminates coating degradation in use**
  - **Lower brightness**
  - **Changes in viscosity**
  - **Odor**

Types of Coating Preservative

- **Only a limited number of preservatives (biocides) approved for food contact in coated paper (FDA 176.170 & 176.180)**
  - **Bromine based biocides (Bronopol)**
  - **Thione**
  - **Benzisothiazalone**
  - **Gluteraldehyde**
  - **Isothiazalone**
- **Different biocides may be combined for maximum biological control**
  - **Quick kill**
  - **Maintenance**

Role of Dyes and Optical Brightening Agents

- Dyes are added to the coating to control its shade
  - Usually blue and black dye used, some red and yellow
  - Dyes lower brightness of coated sheet
- Optical brightening agents
  - Increase the brightness of the coated sheet
    - Molecule interacts with UV light to cause fluorescence of sheet
  - Several types but all work better in presence of carrier such as PVOH
    - Carriers prevent agent from changing to non-fluorescent isomer
    - PVOH used can replace latex in formulation(1:2)