PIMA

Building Leadership Excellence

TAPPI

people resources solutions

Considerations for the Selection of Binder in Double and Triple Coated Systems

Effect of Under Layer Starch Migration on End Use Performance

PaperCon may 2 - 5 2010 atlanta ga

Talent,

Technology and

Transformation

Greg Welsch and **Marianne McKelvy**
Styron, A Division of Dow, Midland, Michigan, USA

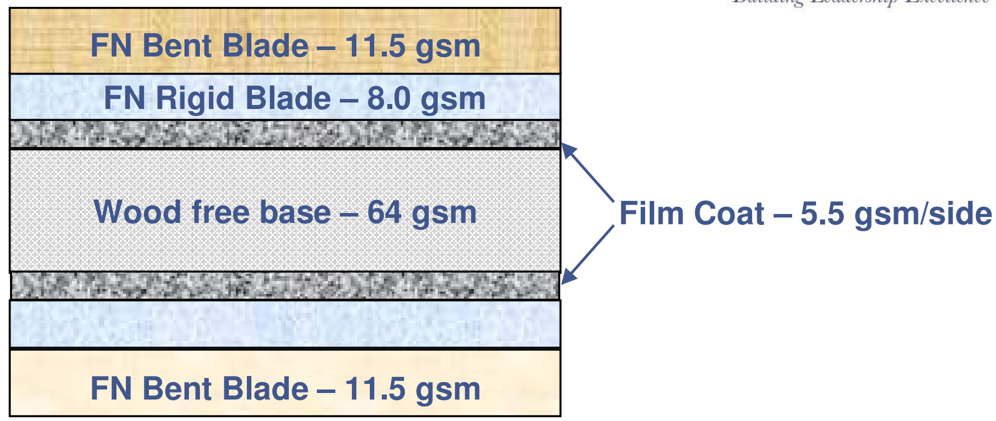
Francis Dobler and **Monika Plass**
Styron, A Division of Dow Europe GmbH, Rheinmuenster, Germany

Dominique Poncelet and **Jean Marbaix**
Burgo Group – Ardennes Mill, Virton, Belgium

Part 1: Triple Coated Wood Free Paper

What did we study?

- **Binding Power (BP)** of latex relative to starch in precoat and middle layer
- **Precoat**:
  - 100 parts coarse $CaCO_3$
  - **Latex & DP starch level variable**
- **Midcoat**:
  - 100 parts coarse $CaCO_3$
  - **Latex & DP starch level variable**
- **Topcoat**:
  - No starch
  - **Gloss and Silk formulations**



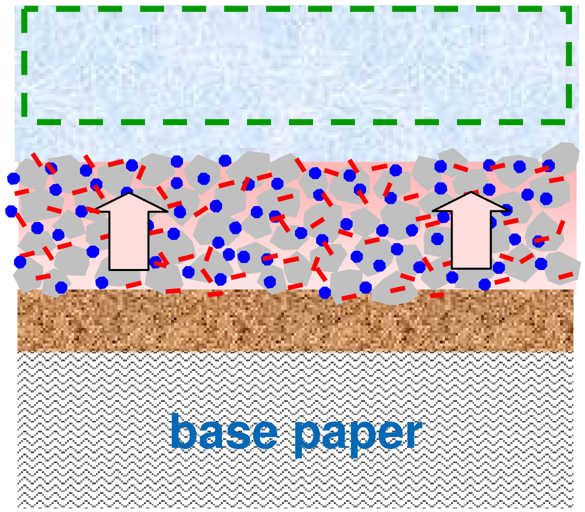
What did we learn?

- Precoat: Latex BP = 2.0 - 2.5 x Starch BP
- Middle layer in glossy grades: Latex BP = 1.6 - 2.0 x Starch BP
- Middle layer in silk grades and uncalendered paper: Latex BP = 1.2 x Starch BP
- High levels of starch used in middle layer significantly slows down ink setting rate
- Supercalendering increases the binding power of under layer latex whereas for starch the binding power is actually decreased.

Part 2: Investigation of Starch Migration

What did we study?

- Hypothesis: Starch migrates from middle layer into topcoat when rewetted by topcoat application
- Analytical technique to measure presence of starch in topcoat
- Technique to quantify amount of starch migrating into topcoat



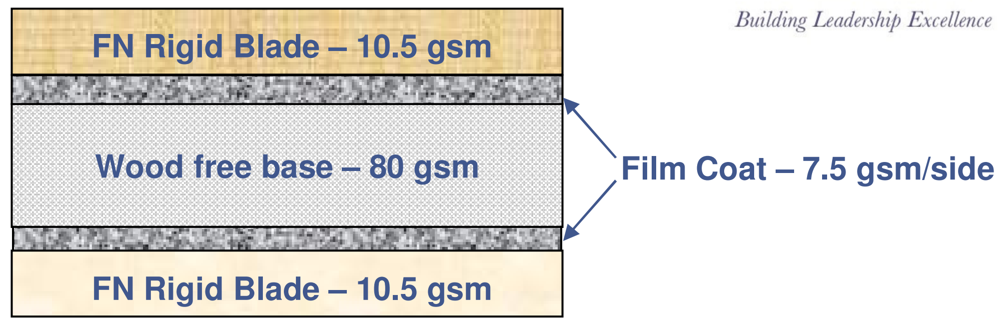
What did we learn?

- Used infrared spectroscopy in surface sensitive ATR mode to detect and measure starch in the topcoat layer
- Starch detected in topcoat remains low for starch levels in middle layer up to 5 parts
- Up to 30-35% of the starch from middle layer can migrate into topcoat
- Accounts for some of the influence of starch in middle layer on end use properties of triple coated paper

Part 3: Double coated wood free paper

What did we study?

- **Precoat**:
  - 100 p coarse $CaCO_3$
  - **Latex & starch level variable**
  - **Starch type variable – TM or HE**
- **Topcoat**:
  - No starch
  - **Gloss, Matte, and Dull formulations**



What did we learn?

- Confirmed similar migration behavior with TM and HE corn starch as w/DP starch
- As starch increased in precoat, more starch was detected in topcoat.
- % of starch migrating into topcoat stayed constant throughout precoat starch dosage range.
  - TM starch: 45-60% of precoat starch migrated into topcoat w/fine pigments and 26-34% migrated into topcoat w/coarse pigments.
  - HE starch: 17-25% of precoat starch migrated into topcoat w/fine pigments and 0-11% migrated into topcoat w/coarse pigments.
- For moderate to high levels of precoat starch, final paper quality was negatively affected:
  - All grades: Increased print mottle, slower ink setting, and more ink required to hit target density
  - Glossy: Lower dry pick strength when starch used induced by calendering process

Part 1: Triple Coated Wood Free

GOALS

- Assess the influence of latex and derivatized potato (DP) starch in pre and middle layers on the properties of triple coated papers
- Investigate the differences in binding power of latex and starch when used in precoat and middle layers
- Investigate glossy and silk grades

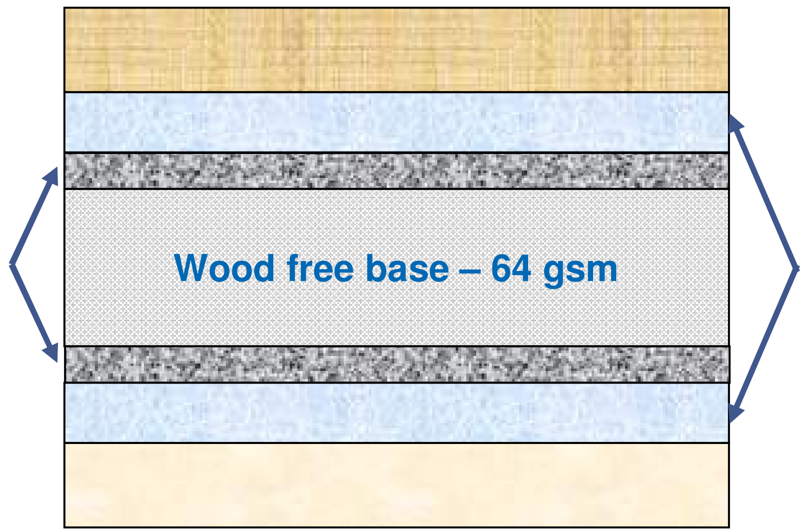
METHOD

- Experimental design and regression modeling
- Variation of latex and starch amounts in pre- and middle-layers
- Two different topcoat formulations with different finishing conditions

Coating Layer Detail

Top Coat: Gloss (felt side)

- 11.5 g/m^2 – FN + Bent Blade
- **Super**calendered



Precoat:

- 4.5 g/m^2 – Film Coater
- 100 parts coarse $CaCO_3$
- **Latex & starch variable**

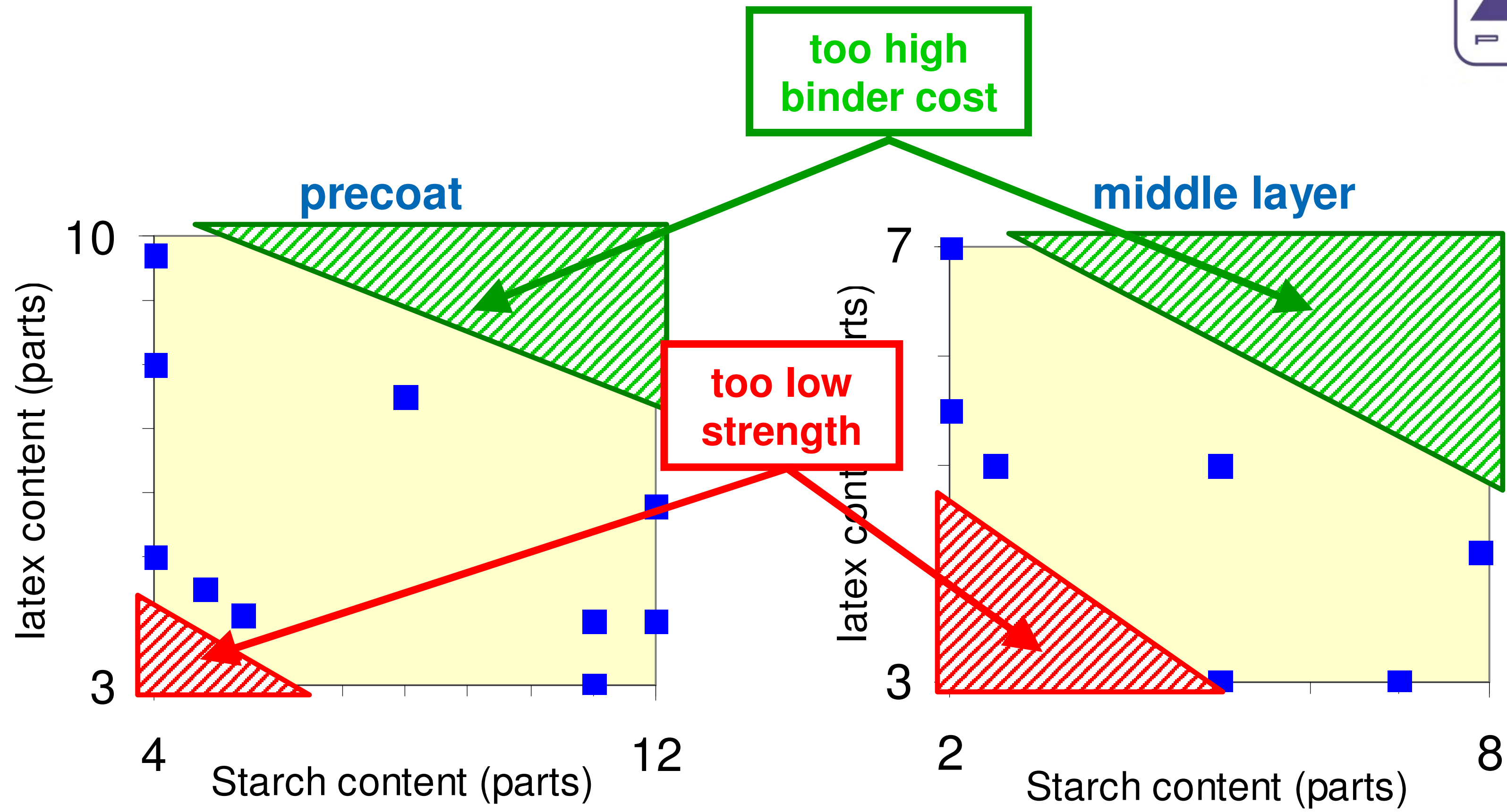
Middle layer:

- 8.0 g/m^2 – FN + Rigid Blade
- 100 parts coarse $CaCO_3$
- **Latex & starch variable**

Top Coat: Silk (wire side)

- 11.5 g/m^2 – FN + Bent Blade
- **Soft** calendered

Starch and latex levels



10 precoat formulations

7 middle layer formulations

13 triple coated trial combinations + repeat of reference

Paper Testing and Data Analysis

Regression analysis

Latex **binding power** → α, γ

Starch **binding power** → β, δ

Paper strength IGT pick

$$\text{Paper strength (IGT pick)} = \text{intercept} + \alpha L_p + \beta S_p + \gamma L_m + \delta S_m$$

S_p and S_m the starch levels in parts in precoat and middle layer

L_p and L_m the latex levels in parts in precoat and middle layer

Latex and Starch “Binding Power”

			Precoat	Middle coat
			binding power ratio latex / DP starch	binding power ratio latex / DP starch
			α / β	γ / δ
Precoat + Middle Coated		IGT pick resistance	1.1	0.8
Triple Coated Glossy	**Un-** calendered	IGT pick resistance	1.5	1.3
	Super- calendered	IGT pick resistance	2.1	2.2
		pass to fail	*high p-value not considered*	1.7
Triple Coated Silk	**Soft-** calendered	IGT pick resistance	2.6	1.1
		pass to fail	2.4	1.2

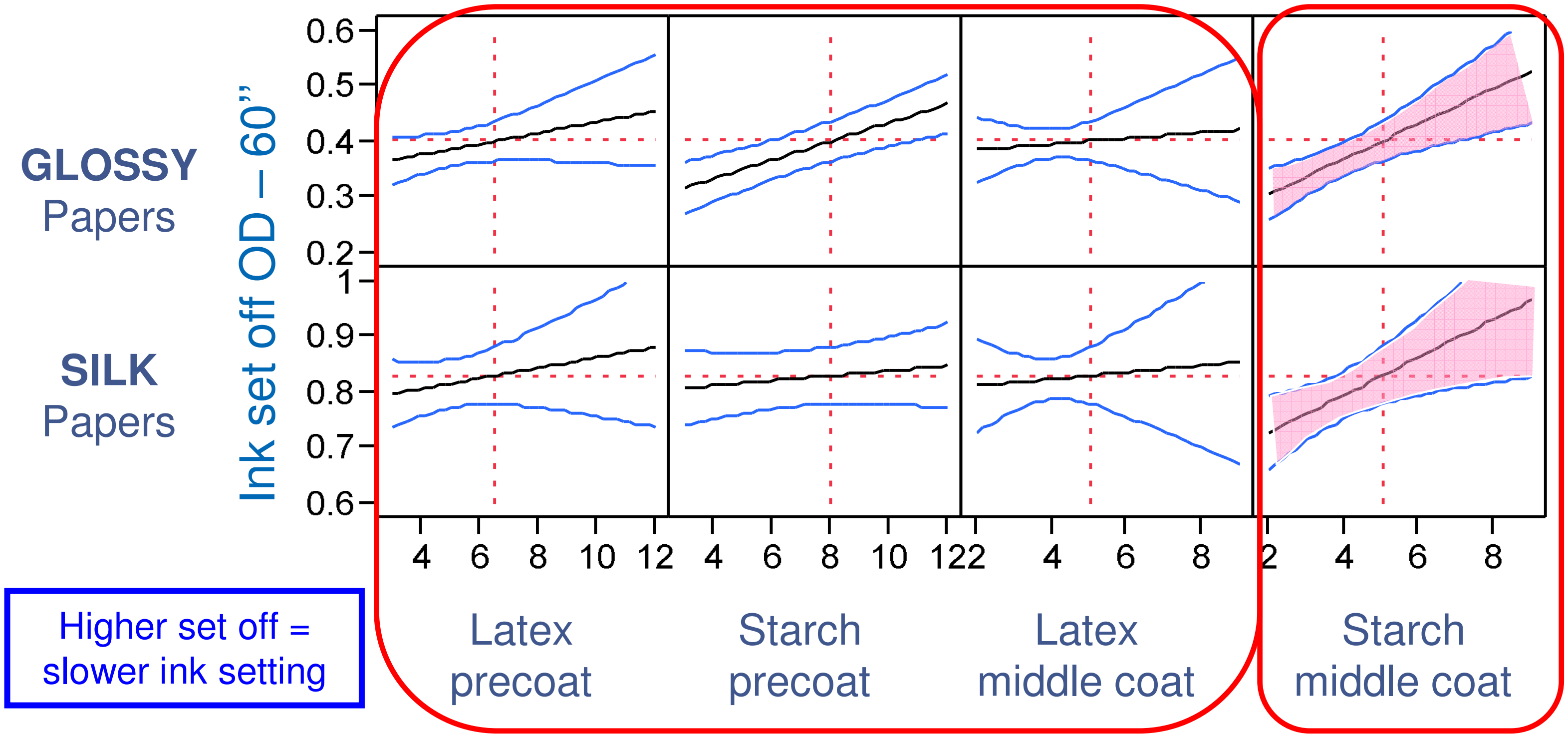
In precoat: latex has about 2.1 to 2.6 times higher binding power than starch

In middle coat:

silk papers: latex has about 10-20% higher binding power than starch

glossy paper: latex has 1.7 to 2.2 times higher binding power than starch

Ink Setting Rate



Ink setting of the triple coated papers was:

- significantly reduced when starch was used in the middle layer
- not influenced by latex in middle layer, or starch or latex in precoat

Impact of Supercalendering on Binder Type

			latex α	starch β	latex γ	starch δ
Triple Coated Glossy	**Un-**calendered	IGT pick resistance	3.38	2.24	3.93	3.04
	Super-calendered	IGT pick resistance	3.8	1.8	5.44	2.52

Supercalendering

increases latex binding power → calender temp **>** Tg of latex — **promotes adhesion of latex particles on pigments**

decreases starch binding power → calender temp **<** Tg of starch — **damages starch film**

Part 1 - Conclusions

Binding power (BP) of latex and starch

- Precoat: Latex BP = **2.0-2.5** x Starch BP
- Middle layer, glossy grades: Latex BP = **1.6-2.1** x Starch BP
- Middle layer, silk grades: Latex BP = **1.2** x Starch BP

Ink setting rate

- Starch in middle layer significantly slows down ink setting of triple coated papers
- Can be an issue for silk and matte grades
- Can limit the amount of starch in middle layer.

Binding power - Effect of supercalendering

- Binding power of latex is increased by supercalendering
- Binding power of starch is decreased by supercalendering

Part 2: Investigation of Starch Migration

GOALS

- Develop hypothesis that explains results from Part 1
- Identify analytical technique that could detect starch in top layer
- Quantification of starch migration into top layer

METHOD

- Infrared spectroscopy (FTIR) in surface sensitive (ATR) mode
- Analyzed coating depth: 2 to 4.5 μm →→ topcoat specific
- Starch absorption band was evaluated at 1150 cm^{-1}
- Develop calibration standards – “known” starch levels in topcoat formulas
- Utilize calibration curve data to quantify amount of starch migration in papers from Part 1

Migration of Starch from Middle to Topcoat

	binding power ratio latex/starch	
	Precoat	Middle coat
	α / β	γ / δ
Pre + Middle coated	1.1	0.8
Triple coated **Un**calendered	1.5	1.3

By application of topcoat layer:

- Binding power ratio increases by ~ 40% in both precoat an middle layer
- Starch in middle layer reduces ink setting rate of topcoat

Hypothesis

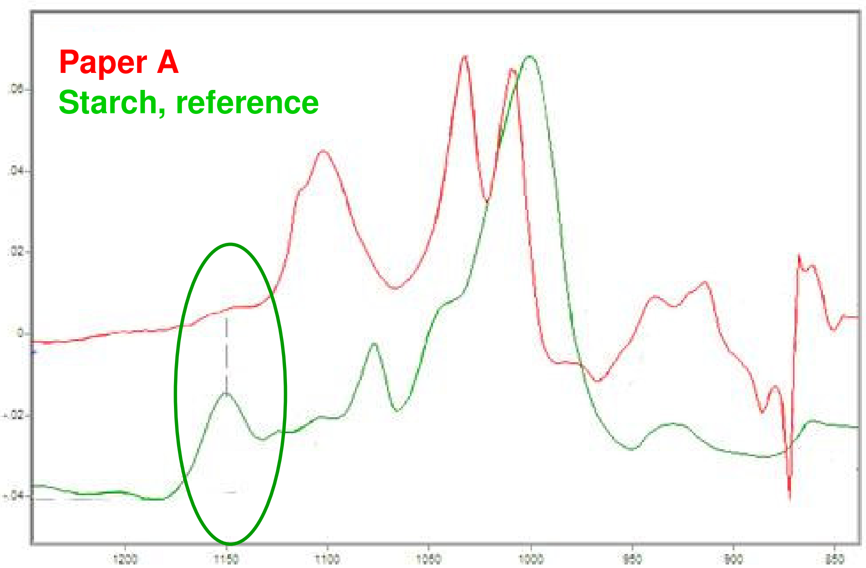
Migration of part of the starch from middle layer to topcoat

Migration of Starch from Middle to Topcoat

Analytical Proof – Detection of Starch in Topcoat

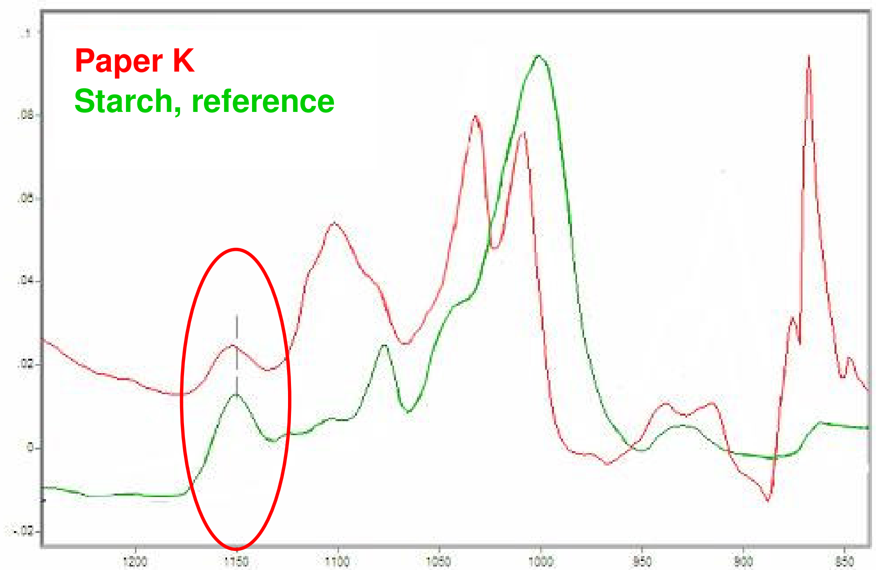
Paper A

- 2 parts starch in middle layer:
- “very weak” starch band



Paper K

- 7 parts starch in middle layer:
- “pronounced” starch band

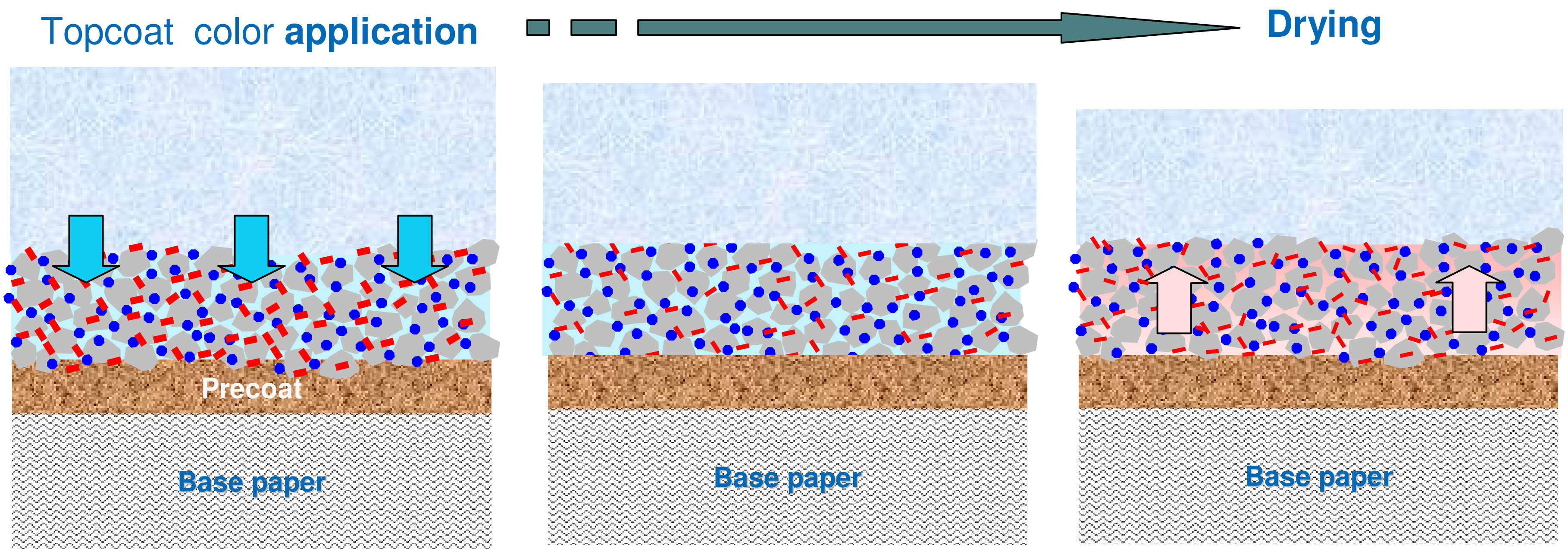


Migration of Starch from Middle to Topcoat

Formulation	A	J	F	I	K
Precoat at 4.5 (g/m^2)	F1	F8	F5	F6	F8
Latex content (parts)	5	4	4.1	7.5	4
Starch content	4	11	5.4	8	11
Middle coat at 8.0 (g/m^2)	F11	F11	F12	F16	F16
Latex content	7	7	3	3	3
Starch content	2	2	5	7	7
Starch level in (g/m^2)	0.15	0.15	0.37	0.51	0.51
Topcoat at 11.5 (g/m^2)					
Estimated starch in topcoat (parts)	starch detected but signal too low to quantify level		0.5	1.6	1.8
Estimated starch in topcoat (g/m^2)			0.05	0.16	0.18
Fraction (%) of starch from middle layer which has migrated in top			15%	32%	36%

- Starch amount detected in topcoat increases with starch amount in middle layer
- Starch content detected in topcoat as high as 1.8 parts
- From 15 to 35% of the middle layer starch migrates into the topcoat
- Starch found in topcoat is low when < 5 parts starch is used in middle layer

Migration of Starch from Middle to Topcoat



Water migrates in middle layer

Water solubilizes part of the starch

Water migrates back into top layer and transports solubilized starch

Part 2 - Conclusions

Starch migrates from middle layer into topcoat when rewetted

- Accounts for some of the influence of starch in middle layer on end use properties of triple coated paper
- Starch content found in topcoat remains low for starch levels in middle layer at < 5 parts
- Starch content in topcoat can be as high as 1.8 parts when 7 parts starch run in middle layer
- Up to 35% of the starch from middle layer can migrate to the topcoat

Part 3: Double Coated Wood Free

GOALS

- Assess the influence of latex and type of starch in precoat layer on the end use properties of double coated papers
- Quantitative comparison of starch migration for two common starch types – hydroxyethylated and thermally modified corn starch
- For gloss, matte, and dull grades

METHOD

- Experimental design and regression modeling
- Variation of latex and starch amounts in precoat
- Variation of starch type in precoat
- Variation of topcoat formulation – glossy, matte, dull

Double Coated Formulations

	Precoat	Topcoat Gloss	Topcoat Matte	Topcoat Dull
Coated side	TS / WS	TS	WS	WS
Calcium carbonate, coarse	100		15	60
Calcium carbonate, fine		70	70	40
High gloss clay, fine		30	15	
High strength SB latex	**variable**	10.5	10.5	10.5
Thermally modified starch	**variable**			
Hydroxyethylated starch	**variable**			
CMC thickener		0.3	0.3	0.3
Solids Content	**variable**	67.5%	68.3%	69.3%
Coating technology	Film coating	Rigid blade	Rigid blade	Rigid blade
Speed (m/min)	915	765	765	765
Coat weight (g/m^2) / side	7.5	10.5	10.5	10.5
Calender Nips / side		4	1	1
Calender Temp (^{o}C)		275	275	275
Calender Pressure (kN/m)		350	60	60

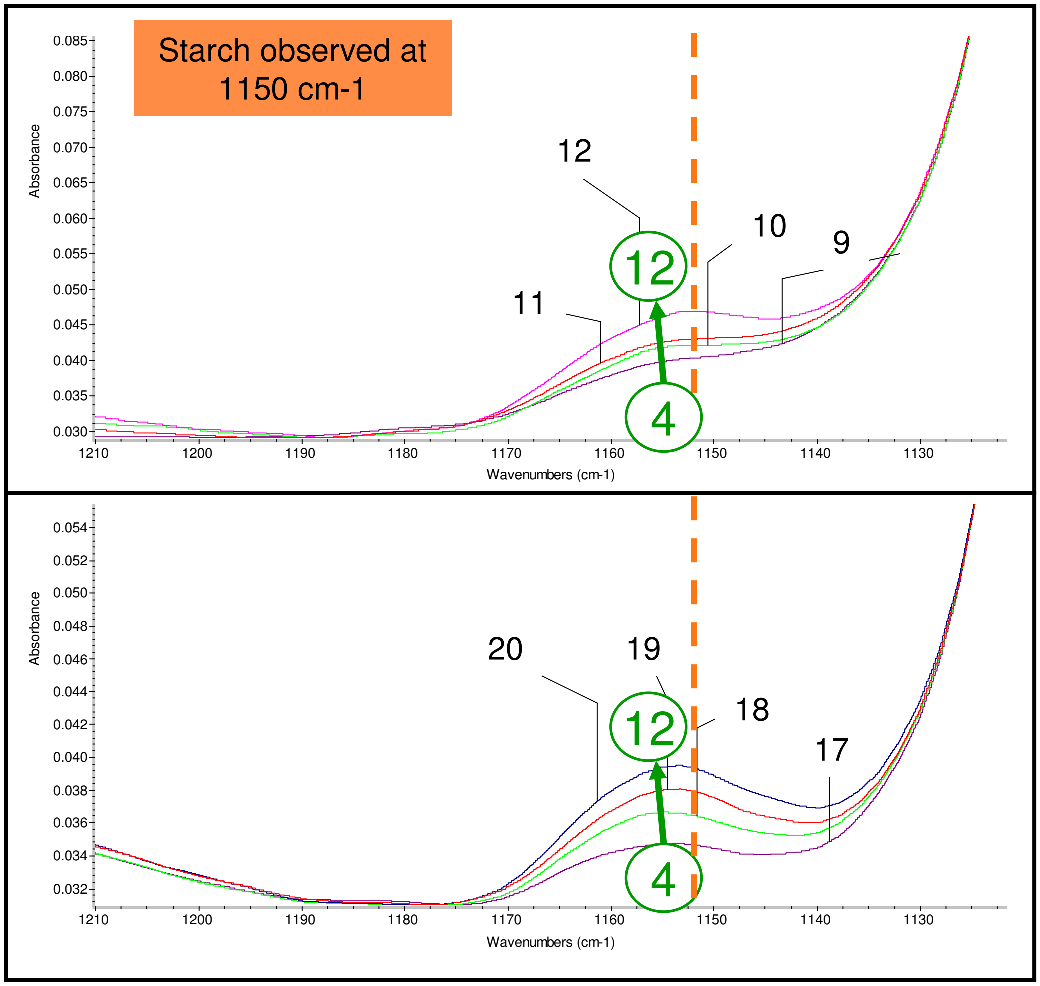
Thermally Modified Starch – Cargill C-Film 7311
Hydroxyethylated Starch – Penford PG 290

Starch and Latex Levels

	Binder	Lowest level	Highest level
Precoat	TM Starch or HE Starch	4	12
	Latex	3	9

Precoat					Top Coat Run #		
Run #	latex	starch	starch	SC	Gloss "I"	Matte "J"	Dull "K"
1	9	4	TM	69.4	9	17	25
2	7	6.7	TM	67.9	10	18	26
3	5	9.3	TM	66.8	11	19	27
4	3	12	TM	65.3	12	20	28
5	5.5	6	TM	68.7	13	21	29
6	6.5	10	TM	66.1	14	22	30
7	9	4	HE	67.6	15	23	31
8	3	12	HE	62.4	16	24	32

FTIR in ATR Mode – Detection of Increasing Starch Content in Top Coat Layer



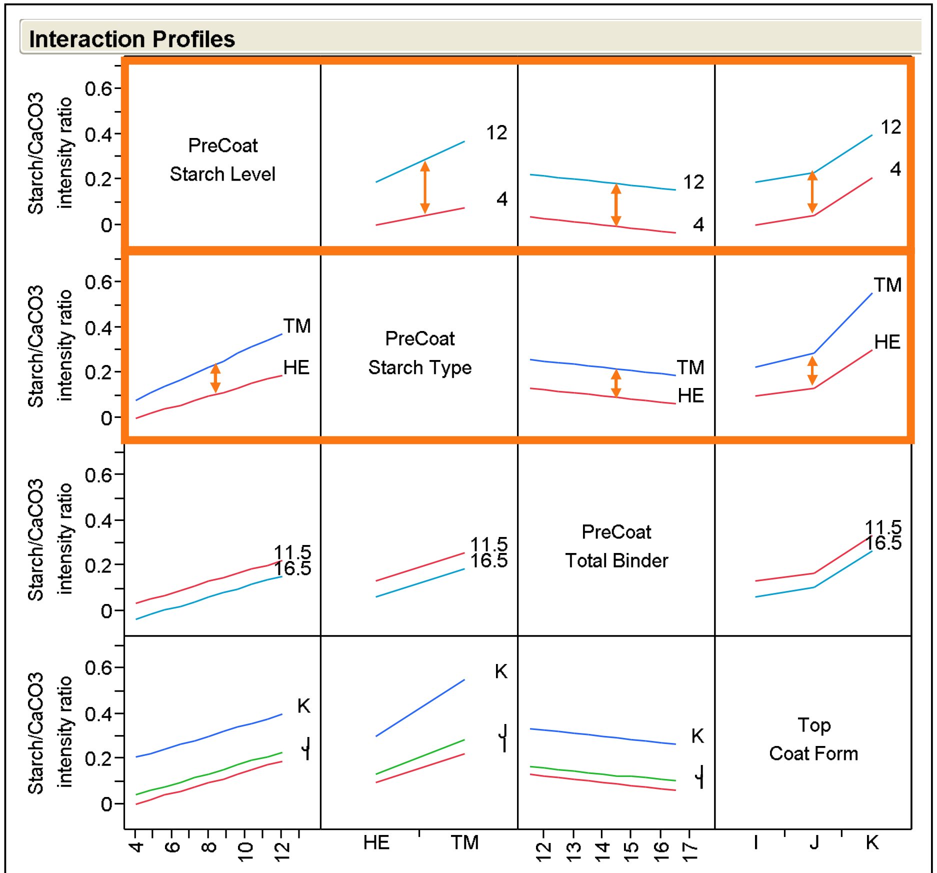
Topcoat "I" - Gloss

- 70:30 - Fine $CaCO_3$/HG Clay
- TM starch in precoat
- As precoat starch increases, more starch detected in top layer

Topcoat "J" – Matte

- 70:15:15 - Fine $CaCO_3$/HG Clay/Coarse $CaCO_3$
- TM starch in precoat
- Increasing starch detection in top layer as precoat starch increases

Quantification of the Starch Amount in Top Coat



Significant terms:	p-value
Pre Coat Starch Level	<0.0001
Pre Coat Starch Type	<0.0001
Top Coat Form	<0.0001
Pre Coat Starch Level * Pre Coat Starch Type	0.049
Pre Coat Starch Type * Top Coat Form	0.038

Summary of Fit
$R2 = 0.97$

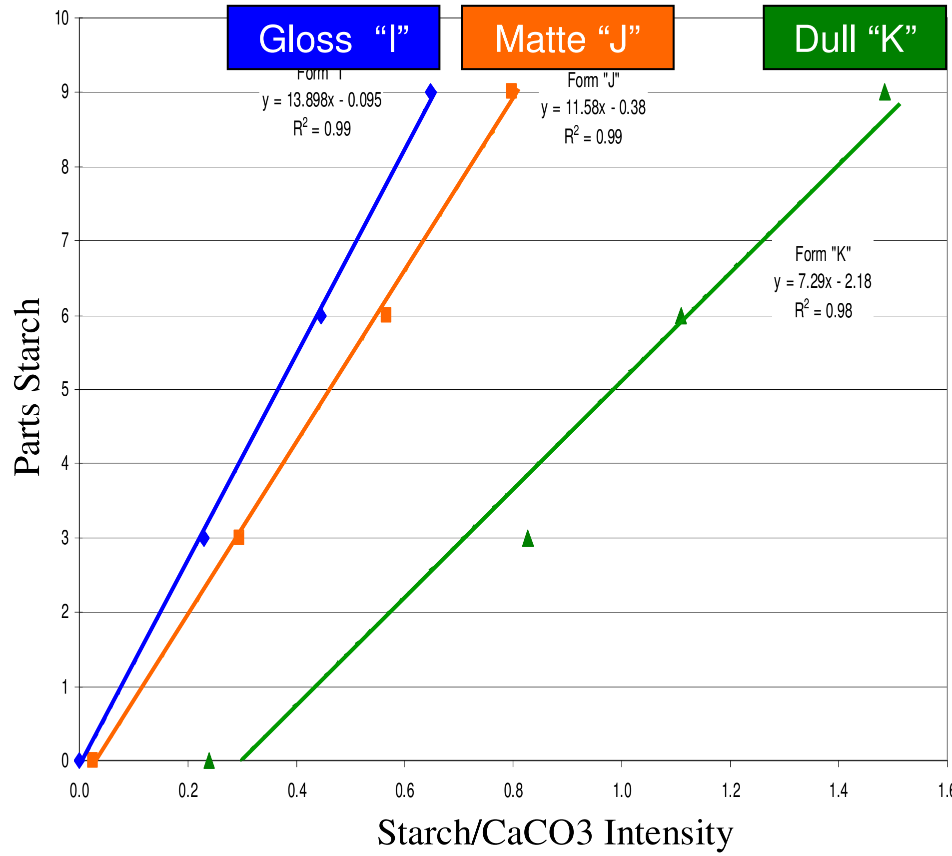
Analysis of Variance
Prob > F = <0.0001

- 1st Order terms: precoat starch level, precoat starch type, and topcoat formulation
- Interaction terms: precoat starch type with precoat starch level and precoat starch level with top coat formula
- Increasing precoat starch level drives higher detection in the topcoat
- TM starch shows ~ 2X more migration than the HE starch

Calibration Standard – TM Starch

Parts TM Starch Versus Starch/CaCO3 Intensity Ratio for Three Topcoat Systems

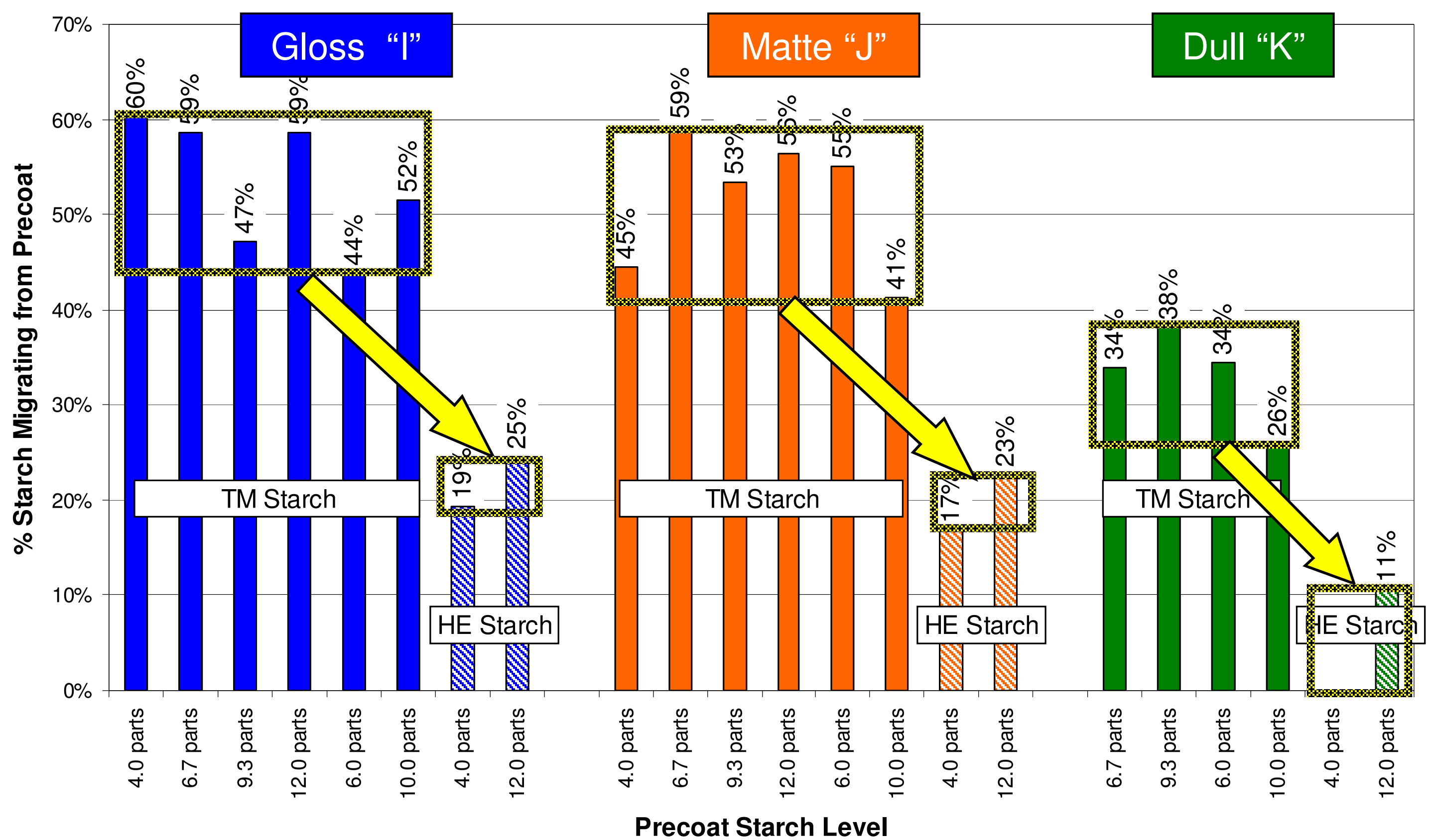
Coating				Run #		
latex	starch	starch	SC	Gloss “I”	Matte “J”	Dull “K”
10.5	0	---	67.5	C1	C7	C13
9	3	TM	66.0	C2	C8	C14
7.5	6	TM	64.5	C3	C9	C15
6	9	TM	63.0	C4	C10	C16
9	3	HE	66.0	C5	C11	C17
7.5	6	HE	64.5	C6	C12	C18



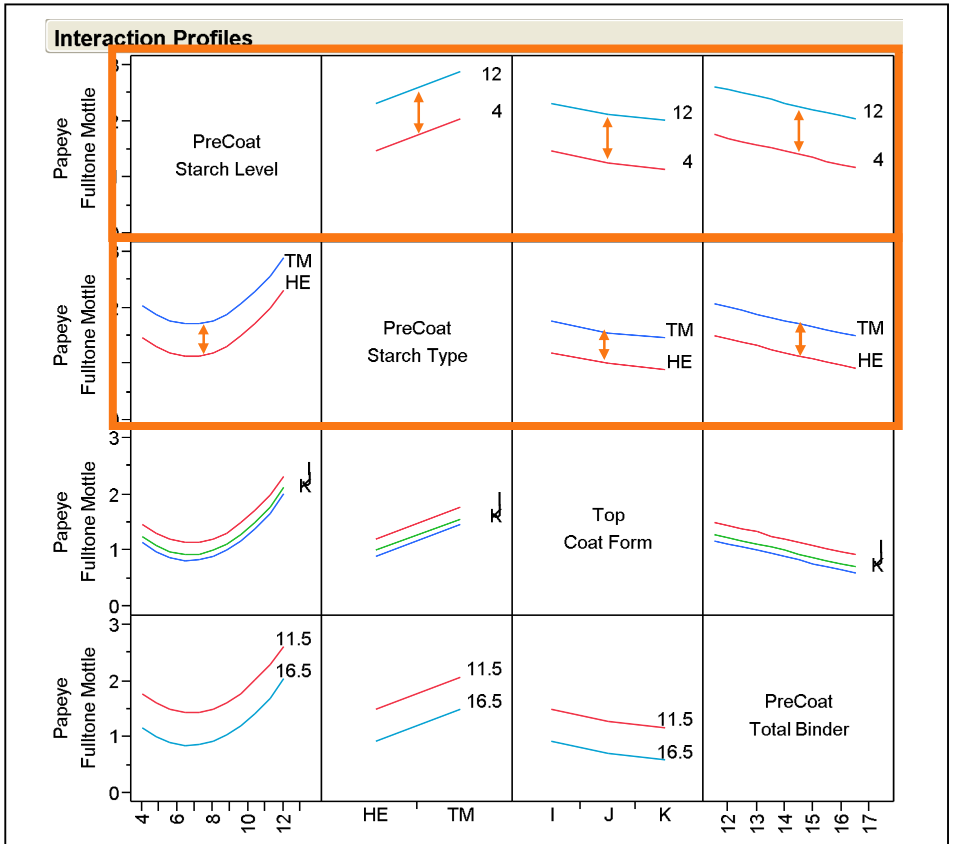
Calibration results utilized to calculate the % starch migrating into topcoat for each topcoat condition.

Calculation Results

% of Precoat Starch Migrating from Precoat Into Top Layer for Three Topcoat Systems



Print Mottle – Full Tone



Significant terms:	p-value
Pre Coat Starch Level	0.0032
Pre Coat Starch Type	0.0084
Pre Coat Total Binder Level	0.0796
Pre Coat Starch Level * Pre Coat Starch Level	0.0040

Summary of Fit
$R2 = 0.70$

Analysis of Variance
Prob > F = <0.0026

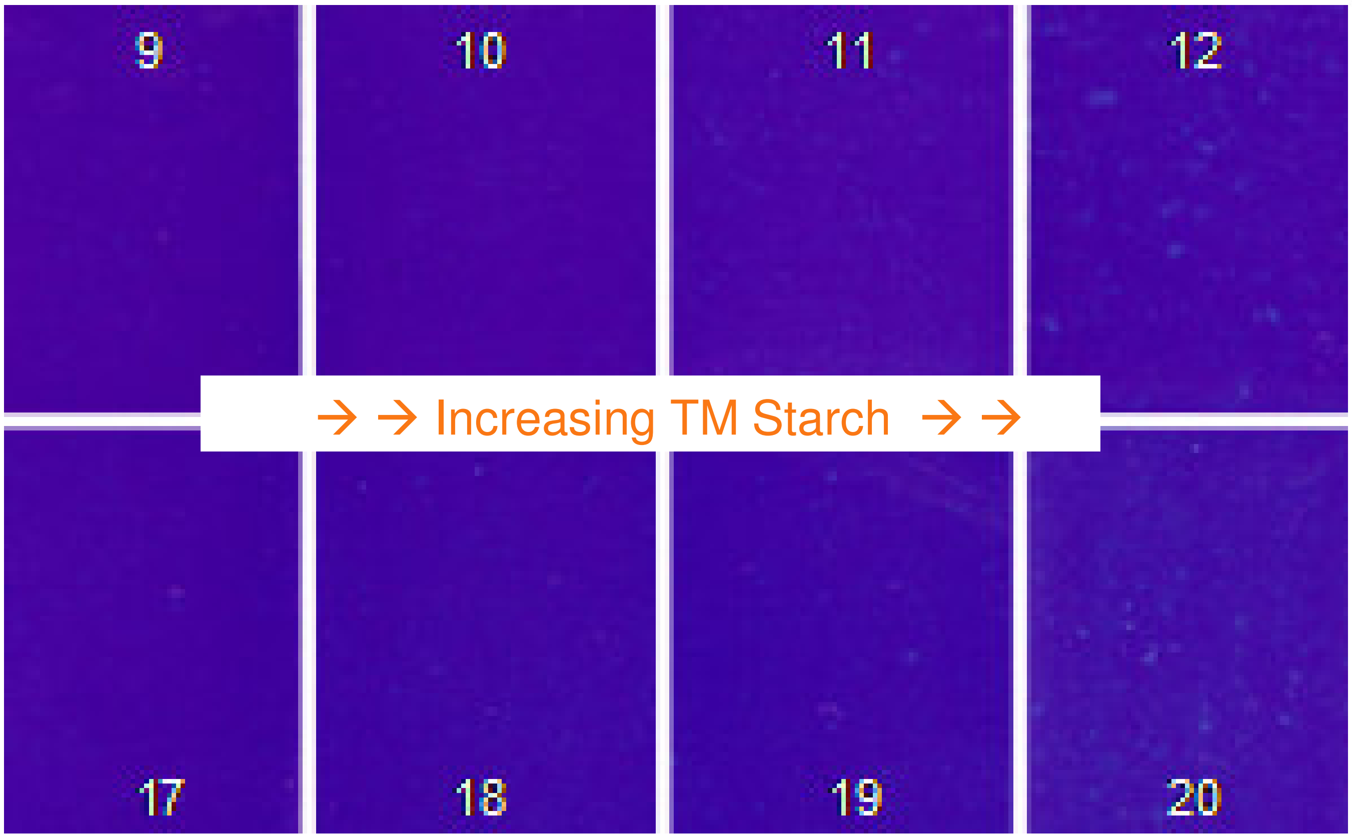
Lower value = lower print mottle

- 1st Order terms: precoat starch level and precoat starch type
- 2nd Order terms: precoat starch level
- Increasing precoat starch level results in more print mottle
- TM starch more prone to mottle than HE starch
- These observations are consistent with starch migration results

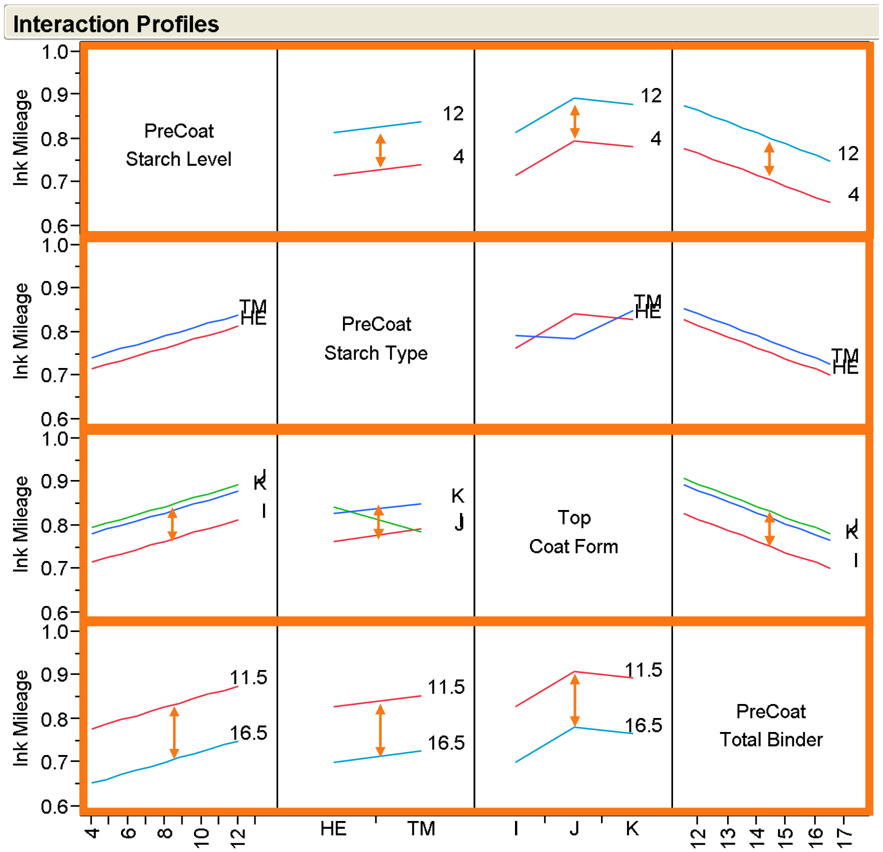
Print Mottle – Full Tone

Top Coat
“I”

Top Coat
“J”



Ink Mileage (amount of ink required to reach target ink density)



Significant terms:	p-value
Pre Coat Starch Level	0.0129
Pre Coat Total Binder Level	0.0091
Top Coat Form	0.0355
Pre Coat Starch Level * Pre Coat Starch Level	0.0509

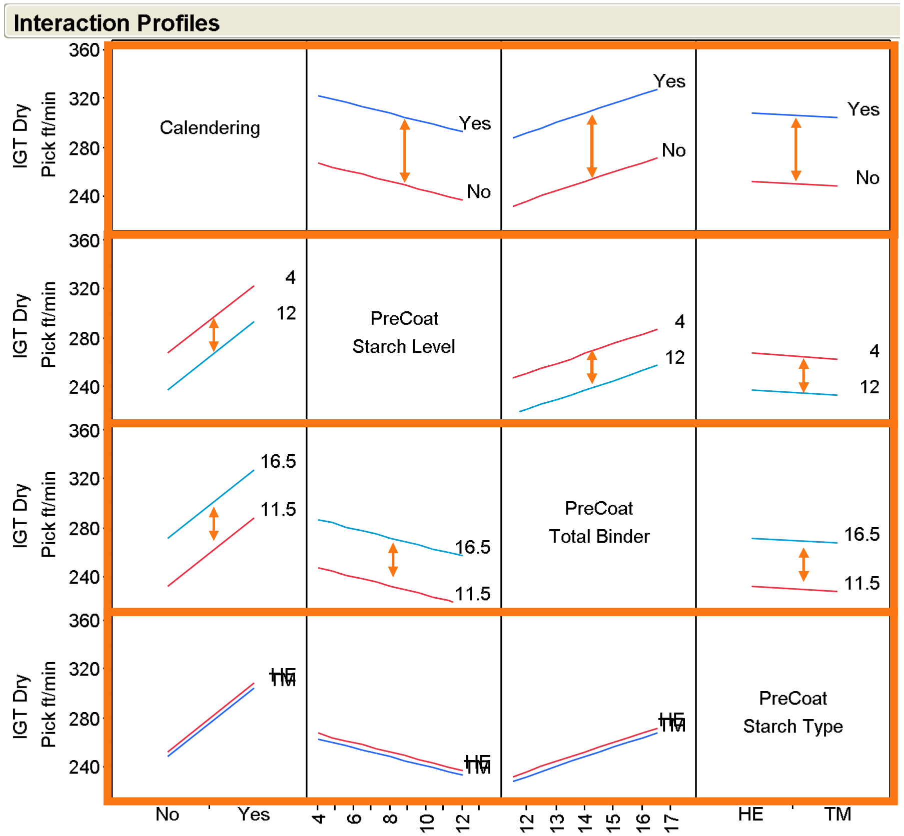
Summary of Fit
$R2 = 0.63$

Analysis of Variance
Prob > F = <0.0099

Lower value = higher ink mileage

- 1st Order terms: precoat starch level, precoat total binder level, and top coat formula
- 2nd Order terms: precoat starch level
- Increasing precoat starch level while reducing latex level results in ~ 17% poorer ink mileage
- Increasing total binder improved ink mileage
- Higher clay topcoat "I" gave better ink mileage
- No significant difference between starch types

Effect of Supercalendering on Strength



Significant terms:	p-value
Calendering	<0.0001
Pre Coat Starch Level	0.1086
Pre Coat Total Binder Level	0.1092

Summary of Fit
$R2 = 0.81$

Analysis of Variance
Prob > F = <0.0006

Higher value = higher pick strength

- 1st Order terms: precoat starch level precoat total binder level, and calendering treatment
- Supercalendering treatment increased dry pick strength
- Increasing precoat total binder improved dry pick strength.
- Increasing precoat starch level while reducing latex level results in lower dry pick strength → Part 1
- No significant difference between starch types

Part 3 - Conclusions

- Confirmed similar migration behavior with TM and HE corn starch as w/DP starch used in part 1.
- As starch increased in precoat, more starch was detected in topcoat.
- % of starch migrating into topcoat stayed constant throughout precoat starch dosage range.
  - TM starch: 45-60% of precoat starch migrated into topcoat w/fine pigments and 26-34% migrated into topcoat w/coarse pigments.
  - HE starch: 17-25% of precoat starch migrated into topcoat w/fine pigments and 0-11% migrated into topcoat w/coarse pigments.
- For moderate to high levels of precoat starch, final quality was negatively affected:
  - All grades: Increased print mottle, slower ink setting, and more ink required to hit target density
  - Glossy: Lower dry pick strength induced by calendering process
- **Multi-Layer systems must be optimized based on final properties, not individual layer results.**

Acknowledgements

- Dow Center of Excellence pilot coater staffs in:
  - Samstagern, Switzerland
  - Midland, Michigan, USA.
- The support of the paper lab technicians
  - North American Paper Expertise Center, Midland, Michigan, USA
  - European Paper Expertise Center, Horgen, Switzerland
- Support from both companies
  - Styron Division - The Dow Chemical Company
  - Burgo Group – Ardennes Mill, Virton, Belgium

Thank you for your attention