

Metered Size Press Coating Formulation Design for Fiber Reduction

Richard Gagnon¹, Jan Walter², Joel Kendrick², Rajan Iyer³, Leslie McLain³, Roger Wygant³

1 - DuPont Soy Polymers
824 Gratiot Street 3RN
Saint Louis, MO 63102

2 - Western Michigan University
4651 Campus Drive
Kalamazoo, MI 49008

3 - IMERYS Clays, Inc.
618 Kaolin Road
Sandersville, GA 31082

ABSTRACT

A major driving force in paper technology development is the reduction in cost of paper production. A primary material cost in the paper production process is wood fiber, the cost of which is increasing rapidly. Reducing fiber usage is difficult, as paper properties are tightly coupled to the amount of fiber. Advances in coating formulation design have begun to show how coatings may be designed for fiber replacement without sacrificing paper properties. Both pigment and binder influence coating mechanical properties. Pigment shapes and sizes, and binder types and amounts are all relevant variables. We report here on combinations of these variables investigated at laboratory and pilot scales. Variations in average coating pigment shape are achieved by varying the ratio between GCC and kaolin, and by varying the platiness of the kaolin. Platier average pigment shape tended to improve stiffness. Many size press binder formulations consist of a sole starch component. Laboratory and pilot scale experiments show synergistic interactions between starch and protein, leading to reduced binder migration into the substrate. Results demonstrate that stiffness and other mechanical and optical properties can be moved above the cubic basis weight dependence on fiber amount with significant potential economic advantages.

INTRODUCTION

As early as 1981, Reinbold and Rohmann identified the possibility of designing coating formulations to improve water resistance and paper stiffness while reducing basis weight for cost reduction [1]. Okomori, et.al., discussed the variation in stiffness with binder type and pigment size and density, and provided a model for mechanical calculations [2, 3]. Gagnon, et.al., explained how pigment size segregation and binder depletion during coating would affect properties such as gloss and stiffness [4]. Jud, et.al., showed how the effects of latex glass transition temperature, coating structures and pigment systems could be used as tools for optimizing stiffness of the composite base paper and coating layer system [5]. Kim-Habermehl described the effects of basis weight, coat weight, formulation, moisture content, binder type, and calendering on stiffness [6]. Toivakka and Bousfield provided a novel micromechanical model to predict mechanical and viscoelastic properties of coating layers [7]. Glittenberg, et.al., used starch and coating color ultrafiltration to improve print gloss, stiffness, mottle and overall printability while increasing the coatweight / basis weight ratio and reducing the total binder level [8]. Morsy and El-Sherbiny studied coating solids, film thickness and plastic pigment effects on the mechanical properties of coated paper [9]. Altemeier, et.al., used size press filling to reduce cost and enhance uncoated freesheet quality, giving energy savings along with improved formation and stiffness [10]. Ratto modeled the mechanical properties of GCC / SB latex coating layers in terms of the latex content and porosity [11]. Lyons discussed work done by Husband using nanodimensional engineering of clay coatings to increase sheet stiffness [12]. Stollmeier, et.al., developed a latex binder that simultaneously optimized metered size press runnability, sheet gloss and paper stiffness [13]. Mathur developed a novel fibrous filling pigment that provided improvements in bulk and stiffness while reducing wood fiber [14]. Gisella and Laufmann used a pigmented starch size press application to add a small amount of surface pigment while maintaining stiffness and strength [15]. Sajbel discussed a wide variety of surface sizing additives, including GCC, and their effect on printability stiffness [16]. Husband, et.al., have examined the effects of pigment shape on the in-plane and out-of-plane tensile properties of freestanding pigment coating films [17-19].

Recent trends in papermaking show that papers, both coated and uncoated, have become brighter, bluer and lighter in basis weight. This is expected to continue in the foreseeable future, as fiber costs have increased significantly and papermakers are struggling to improve quality while maintaining costs. An interesting area of development work is fiber reduction while keeping optical and surface properties the same. Typically, replacement of fiber in uncoated paper is achieved with pigments either as filler or in pigmented sizing formulations. However, when pigments are added to the paper at the expense of fiber there is almost always a penalty in terms of paper stiffness.

In uncoated freesheet applications the typical mineral used is either precipitated calcium carbonate or ground calcium carbonate. These are low aspect ratio pigments or agglomerates. Addition of kaolin is not usually acceptable due to brightness and shade considerations. However, research done at Imerys has shown that high aspect ratio, or platy, kaolins provide significant in-plane directional modulus improvements. The current extension of this work is to evaluate minimal levels of platy kaolins in combination with ground calcium carbonate for practical applications as a freesheet surface treatment, thereby minimizing deleterious effects on final sheet brightness and color while maximizing stiffness development.

Bench scale work done at DuPont Soy Polymers laboratories has shown significant rheological synergy in blends of starch and soy proteins. Existence of this synergy is not obvious from knowledge of the individual components. The rheological synergy has led to improvements in size holdout in laboratory experiments and limited mill trials.

A natural extension of these different avenues of research is to apply minerals in conjunction with protein and starch to paper and observe the change in paper stiffness. Thus, this work was aimed at applying combinations of platy kaolins and ground calcium carbonates while also varying amounts of protein and starch using a pilot scale metering size press. The tests on the 'coated' paper demonstrate the impact of the various pigments and binders on paper properties, and suggest the possibility of a significant degree of fiber replacement resulting in overall lower costs for the paper producer.

This work used a metered size press (MSP) applicator for the wide range of coat weight targets and coating solids anticipated. It was felt that the MSP would provide greater coating holdout than either a puddle size press or any blade applicator. Greater holdout should enhance the mechanical I-beam effect of the coating on the basestock. It is understood that other types of applicators could potentially be used. MSPs are widely available throughout the industry, giving this work broad applicability.

THEORY

Out-of-plane bending resistance (S_b) is a function of paper thickness (d) and elastic modulus (E). A simple expression including these parameters is given as

$$S_b = (E d^3)/12 \quad (1)$$

Similarly, we may express bending stiffness as a function of basis weight

$$S_b \sim E b^3 \quad (2)$$

From both Eqs. 1 and 2 we see that a reduction in fiber will produce a decrease in bending resistance. By placing a reinforcing layer with a high elastic modulus at the surface of the paper web, however, increases in resistance to bending may be obtained.

Lepoutre and Rigdahl examined the applicability of composite theory to this problem and found that good agreement could be reached between measured and calculated values of elastic modulus for pigmented coating films [20]. Through an application of the Halpin-Tsai equations, it was shown in that work that pigments with higher shape factor would be expected to increase elastic modulus through distribution of stress throughout the reinforcing plane. They postulated that this likely resulted from a higher degree of pigment orientation in the plane. Most typical paper coatings have very low binder volume fractions (ca. 20 – 26%) and the influence of porosity on elastic modulus must also be taken into consideration.

In the experiments reported here, surface treatments were either clear (unpigmented) sizing or were sizing with very high (45 – 63%) binder volume fractions. The effect of porosity is considered far less important than the location of pigmented size with respect to the neutral plane and the relative degree of film continuity. We have postulated that by increasing application solids and through the incorporation of soy protein we could develop a more highly localized sizing film at the surface of the sheet and maximize its contribution to the bending resistance of the paper web.

EXPERIMENTAL RESULTS AND DISCUSSION

Laboratory Scale Binder Rheology Experiment

A laboratory experiment was performed at the DuPont Soy Polymers laboratory in St. Louis, MO to examine the effects of blending starch and protein. In this experiment, clear sizing solutions were made with varying ratios between starch and protein. A variety of rheological measurements were performed on these solutions. Figure 1 shows the $\tan(\delta)$ as a function of the oscillatory frequency of the applied stress for a selected set of different size solutions. The δ is the phase angle between an oscillatory strain driver signal and the viscoelastic stress response of the media. It is generally accepted that lower values of $\tan(\delta)$ indicate greater elastic energy storage. Two of the solutions illustrated contained 0% starch and 100% starch while a third had 80% starch. In the absence of any interaction between the starch and protein, it might be assumed that the 80% solution would fall between the 0% and 100%. However, it can be seen that the $\tan(\delta)$ for the 80% solution was much lower than that of the pure solutions. This could not have been predicted from knowledge of those pure systems. It is indicative of the formation of a solution molecular structure, dependent upon the relative concentration of the two types of molecules, capable of storing a greater amount of elastic deformational energy than a pure solution of either of those types of molecules.

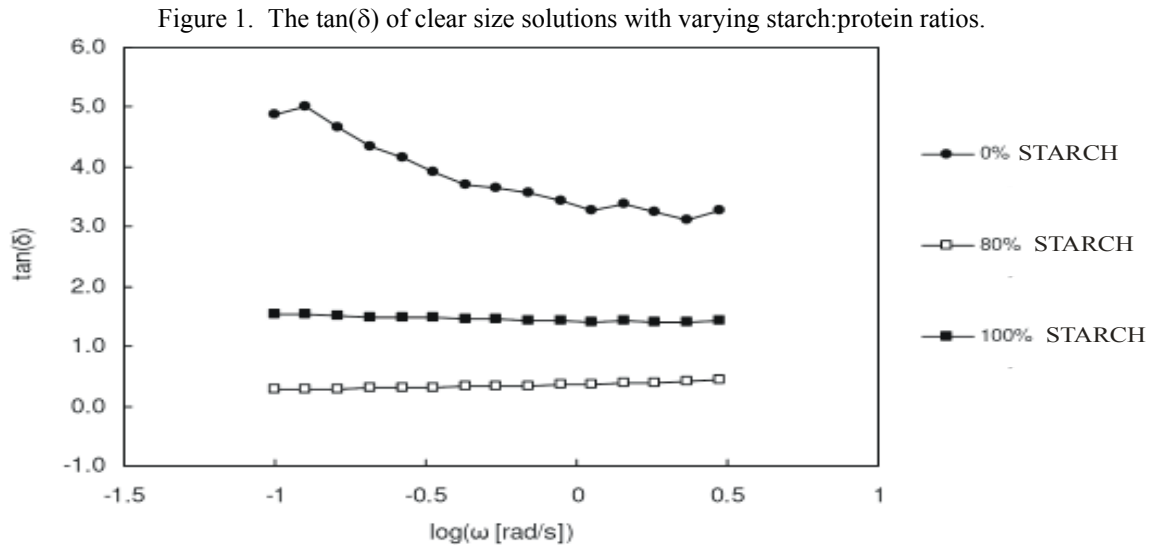


Figure 2 illustrates the yield stress for a full range of clear size solutions with starch:protein ratios varying from 0:100 to 100:0. This data unambiguously demonstrates the statistically significant variation of the strength of the solution molecular structure with the ratio between the two dissimilar molecular types. It was hypothesized that the strength of this solution molecular structure could have a significant influence on the holdout of size solutions in paper coating applications.

Laboratory Scale Pigment Screening Experiment

A laboratory experiment was done at the IMERY'S Paper Technology Center in Sandersville, GA as a screening experiment for a pilot coater trial. A particular concern when kaolin is used to coat a high brightness freesheet basestock is that kaolins are typically somewhat yellow in comparison to both the basestock and the calcium carbonates used as fillers in these grades. Part of the laboratory scale work looked at kaolins with different Hunter b values (higher b values indicate greater yellowness). Those kaolins also had different degrees of platiness. The platiness, or kaolin shape factor, was measured using a patented technique [21]. Physical properties of the pigments used in this laboratory experiment are provided in Table I. The pigment physical property variations were expected to influence size holdout and stiffness. In addition to the grades of kaolin and GCC, the ratio between the kaolins and GCCs was also varied. In this experiment, the binder system was held constant. The coating formulation matrix is given in Table II. Coatings were applied by hand drawdown using wirewound rods onto 92 brightness, 20# office copy paper. Coatweights were 2 and 4 g/m². Coated strips were calendered at room temperature using a single steel nip between 15.2 cm (6") rolls at 7.6 m/min. (25 ft./min.) with a lineal pressure of 30.8 kN/m (176 pli).

Figure 2. Yield stress of clear size solutions with varying starch:protein ratios.

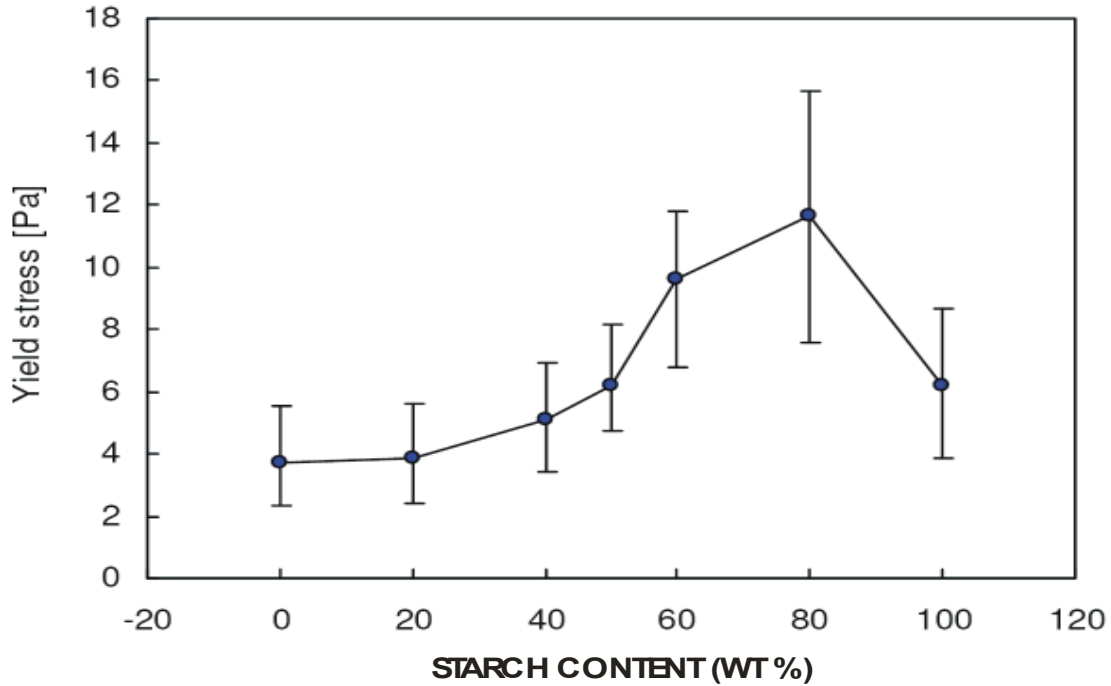


Table I. Physical Properties of Pigments used in Laboratory Pigment Screening Experiment.

Pigment ID	GCC1	GCC2	KaolinA	KaolinB
Brightness	96	97	88	90
b Value	0.1	0.2	3.1	2.2
Mass % finer than 2 um ESD	87	60	89	96
Mass % finer than 0.25 um ESD	21	12	34	49
Shape Factor	*	*	58	32

Table II. Coating Formulation Matrix for Laboratory Pigment Screening Experiment.

Coating #	1	2	3	4	5	6	7	8	9	10	11	12
GCC1	50	50	0	0	70	70	0	0	85	85	0	0
GCC2	0	0	50	50	0	0	70	70	0	0	85	85
KaolinA	50	0	50	0	30	0	30	0	15	0	15	0
KaolinB	0	50	0	50	0	30	0	30	0	15	0	15
Starch	20											
Protein	5											

A small number of primary sheet properties were measured for this experiment. Decisions derived from these results were based primarily on the brightness, color, whiteness and bending resistance (TAPPI Test Method T556). These results are shown in Table III for the lighter coatweight. Trends were similar for the heavier coatweight. Optical data were used to eliminate KaolinA and coatings with 50 parts of KaolinB from consideration. Bending resistance data showed that more than 15 parts of kaolin were required to improve stiffness. At the intermediate GCC:clay ratio of 70:30 with KaolinB, GCC1 provided marginally superior bending resistance in comparison to GCC2. Thus, the pigmentation for pilot scale work was chosen to be 70 GCC1:30 KaolinB.

Table III. Laboratory Pigment Screening Experiment Primary Results.

Coating #		1	2	3	4	5	6	7	8	9	10	11	12
Brightness	Mean	94.59	94.79	94.42	94.71	94.90	95.04	94.75	95.07	95.15	95.34	94.94	95.12
	90% Conf.	0.13	0.08	0.09	0.10	0.06	0.10	0.11	0.09	0.04	0.03	0.08	0.09
Hunter b	Mean	-7.07	-7.08	-6.80	-7.09	-7.03	-7.28	-6.98	-7.35	-7.35	-7.41	-7.20	-7.39
	90% Conf.	0.11	0.10	0.14	0.08	0.11	0.05	0.13	0.06	0.05	0.03	0.07	0.07
Whiteness	Mean	122.3	122.6	121.1	122.5	122.5	123.6	122.2	123.9	124.0	124.4	123.2	124.1
	90% Conf.	0.5	0.4	0.6	0.4	0.5	0.3	0.5	0.2	0.2	0.1	0.3	0.3
Geometric Mean Bending Resistance (mN)	Mean	11.9	14.4	13.4	13.6	14.8	14.0	14.7	13.4	12.3	11.7	13.4	12.6
	90% Conf.	0.6	0.6	0.6	0.7	0.5	0.3	1.0	1.1	1.2	0.3	1.0	0.9

Pilot Coating Trial

All pilot coating work was performed at Western Michigan University's Pilot Plant. The basestock used was a 60# freesheet offset grade produced using only water on the commercial paper machine's size press. This basestock had about 16.5% ash, with almost 15% being CaCO₃ (as determined from multiple temperature ashing). Coatings were applied using the rod metered size press. Grooved rods (IPI 004, 0.001537 in²/in) were used with three different rod pressures to achieve coatweight ramps. All coatings were applied at 308 m/min. (1000 ft./min.) with online steel-to-steel calendering at 78.8 kN/m (450 pli) and ambient temperature. Coating formulations used are shown in Table IV. In formulations with protein, the protein amount used was chosen to replace starch on an equal volume basis. As mentioned above, the pigment blend consisted of 70 parts of GCC1 and 30 parts of KaolinB. Coater conditions, including coating solids, temperature and viscosity, are shown in Table V.

Table IV. Coating Formulation Matrix for Pilot Coating.

Material	Clear Size, Pigment Volume Fraction = 0		Pigment Volume Fraction ca. 0.37		Pigment Volume Fraction ca. 0.55	
	Reference	Trial One	Trial Two	Trial Three	Trial Four	Trial Five
Starch	100	80	100	80	50	40
Protein	0	16.8	0	16.8	0	8.4
Pigment Blend	0	0	100	100	100	100

Table V. Pilot Coater Conditions

Coating ID	Coating Properties				Machine Variables			Results	
	Solids	Viscosity	Temp.	pH	Floats	Infra-Red	Rod Pres.	Coat Wt.	Moisture
	%	cP	°C		°C	°C	10 ⁵ N/m ²	g/m ²	%
Reference 100 Starch	10.1	57	47	*	111	982	1.4	2.1	5
							2.1	1.4	4.8
							2.8	1.0	*
80 Starch 16.8 Protein	10.0	55	37	9.2	111	982	1.4	2.0	6.3
							1.7	1.4	5.1
							2.1	1.0	4.5
100 Starch 100 Pigment	20.2	143	38	8.5	96	760	1.4	5.0	6
							1.7	4.6	5.3
							2.1	4.1	4.8
80 Starch 16.8 Protein 100 Pigment	19.7	134	41	9.6	96	760	1.4	5.2	6.1
							1.7	4.7	5.2
							2.1	4.2	4.5
50 Starch 100 Pigment	26.5	212	46	8.9	96	760	1.4	7.3	5.3
							1.7	6.8	4.5
							2.1	6.2	4
40 Starch 8.4 Protein 100 Pigment	26.0	216	42	9.3	96	760	1.4	8.1	5.5
							1.7	7.5	4.5
							2.1	7.0	4

The coating formulations in Table IV and coater conditions in Table V originated from a Plackett-Burman screening design. A primary variable was binder type; starch only and starch plus protein. The design was expanded to three levels of pigment volume fraction and three coatweight levels. Run order was not randomized. Gas fired infra-red and air flotation dryers brought the moisture to the levels reported in Table V. The IR dryers had four burners, two on each side of the sheet, arranged in two banks. All burners were at the same temperature for each run.

A large number of response variables were measured on the coated paper samples. Measurement results are provided in the Appendix for interested readers. Response surface regression analyses were conducted for all of the response variables using StatSoft Statistica. A computational mode, “Best Subsets,” was used in which regression terms are chosen so as to maximize the adjusted R^2 value. The adjusted R^2 is adjusted to take into account the number of degrees of freedom used by the regression model. Using this statistic to optimize the regression helps to minimize the number of terms included in the model. Each regression considered more than 300,000 possible models based on six independent variables. The six variables were the starch level, protein level, pigment level, total basis weight, coatweight and total ash level. Each independent variable was considered in linear and square powers and in cross terms with every other variable. All possible combinations of all of these linear, square and cross terms were tried for each response variable, these combinations making up the 300,000 or so possible models considered. All of the regressions gave statistically significant fits (at a 5% significance level).

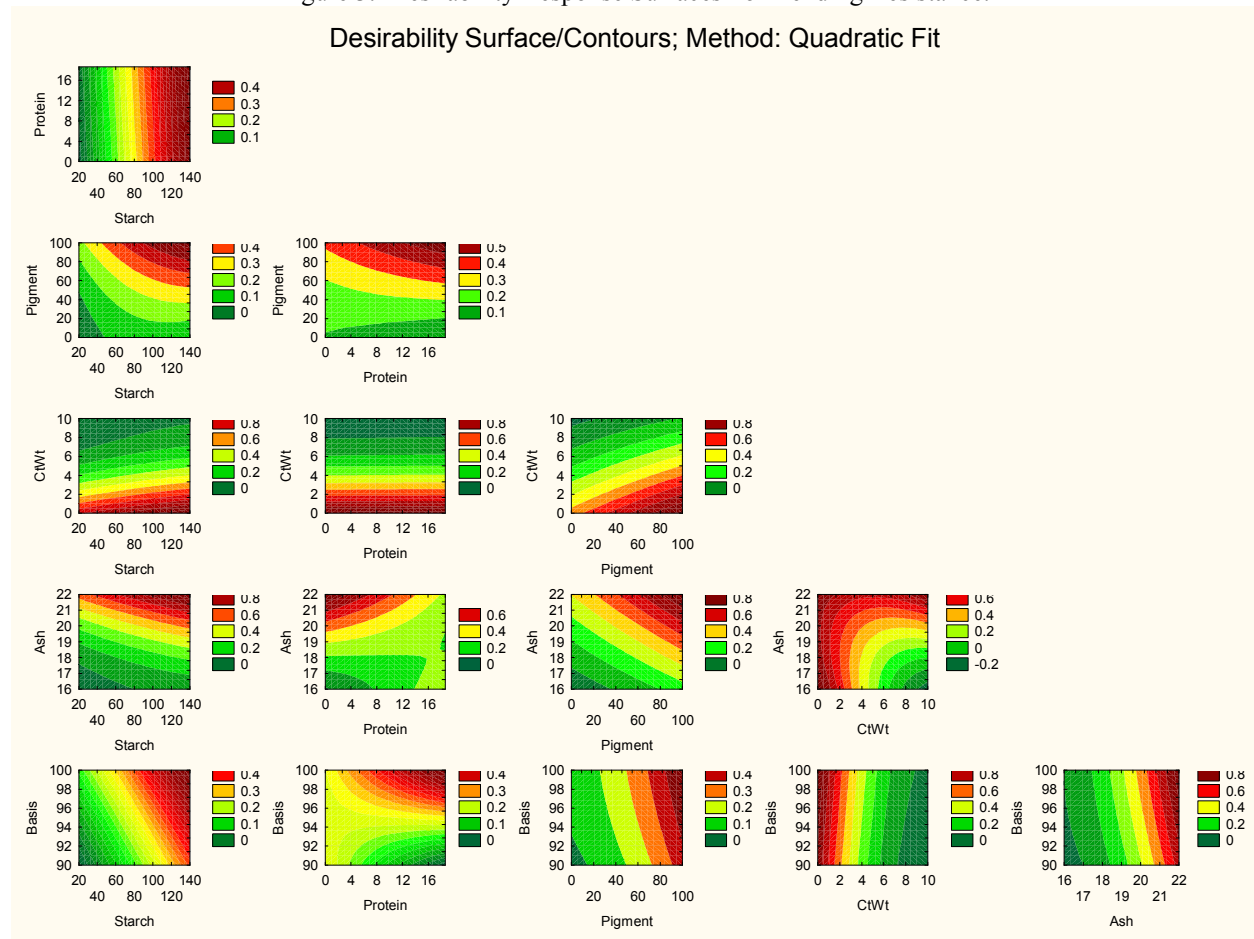
Table VI presents an attempt to summarize results of the regressions. The third column in the table, with the title “D o G,” gives the “Direction of Goodness” assumed for the response variables. For example, for Hunter b or F8 Absorption, reductions in value have been treated as desirable. Note that in some circumstances, the directions of goodness assumed for particular responses may need to be reversed. In this table, a “+” signifies that the independent variable had a desirable influence on the response variable, whereas a “-” indicates an undesirable influence. An “=” indicates little or no influence. A “+/-” indicates that the independent variable gave mixed responses, perhaps with saddle points in some of the response surfaces.

Table VI. Summary of Response Surface Regression Results.

Influence on Desirability	Adjusted R^2	Do G	Starch	Protein	Pigment	Coatweight	Ash %	Basis Weight
Geometric Mean Bending Resistance	0.86	+	+	+/-	+	-	+	+
Burst	0.88	+	+/-	+/-	-	+/-	=	+
Scott Bond	0.86	+	+	=	-	+	+	+
IGT Dry Pick	0.99	+	+	-	+	+	=	-
Linting	0.48	-	+	+	+	-	+	+
Caliper	0.83	+	=	=	+	-	+	+
Bulk	0.94	+	=	=	+	-	+	-
Low Pressure Gurley Air Permeability	0.99	+	-	+/-	+	+	-	-
Parker Print-Surf S10 Roughness	0.75	-	+	+	-	+	+/-	+/-
Sheffield Roughness	0.82	-	=	=	+	+	=	=
Static Coefficient of Friction	0.58	+	+	+/-	+	-	-	+
Kinetic Coefficient of Friction	0.56	+	-	+/-	+	-	-	+
Brightness Mottle % Contrast	0.99	-	-	=	+/-	+	-	=
Paprican Microscanner Formation	0.97	+	=	=	+/-	+	+	=
Dry Prufbau Magenta Heatset Print Density	0.71	+	-	+	-	+	+	+
Ink Setoff	0.51	+	-	-	+	-	+/-	-
Croda Redwipe % Contrast	0.99	-	-	-	-	-	-	=
Croda Redwipe 8 bit Graytone	0.99	+	+/-	-	-	+	+	=
Hercules Size Test	1.00	+	-	+	-	=	+	+
Brightness	0.97	+	-	+/-	+	-	=	+
Opacity	0.85	+	=	+/-	+	+/-	+	+
Hunter b	0.99	-	+	+/-	+	-	-	=
Fluorescence	0.88	+	+	=	-	+	+	-
Whiteness	0.97	+	+/-	+/-	+	-	-	=
Sheet Gloss	0.91	+	=	=	+/-	+/-	-	=
Print Gloss	0.81	+	=	+/-	-	+	-	-
Delta Gloss	0.92	+	=	+/-	-	+	=	-
F8 Scatter	0.90	+	+/-	+	+	-	+	-
F8 Absorption	0.66	-	=	+/-	+	+	-	+
F10 Scatter	0.93	+	-	+/-	+	-	-	-
F10 Absorption	0.94	-	-	-	-	=	-	+
Basis Weight Normalized Opacity	0.76	+	-	+	+	-	=	

Figure 3 illustrates desirability surfaces for the geometric mean of the bending resistance. It is this type of display that was used to develop the qualitative information displayed in Table VI. Each of the individual surfaces in Figure 3 represents the response of Bending Resistance to two different independent variables. For example, in the bottom row of plots, all of the Y axes represent Basis Weight, while the X axis is different for each plot. Similarly, for the left hand column of plots, all of the X axes represent starch content level in the coating formulations. Pigment content level is the Y axis for the second row of plots, then flips over to become the X axis for the third column of plots. For each plot, the scale goes from green being least desirable to red being most desirable. In the five plots involving protein level, two have saddle points, one shows no response to protein level, and two show positive responses to protein level. Thus, protein is assigned a “+/-” qualitative effect on bending resistance. All five plots involving pigment level show an increase in desirability with increasing pigment level, thus pigment is assigned a qualitative “+” effect on bending resistance.

Figure 3. Desirability Response Surfaces For Bending Resistance.



To summarize the summary presented in Table VI, consider assigning a value of 0 to “=” and “+/-” responses, -1 to “-” responses and +1 to “+” responses. Doing this shows that starch (-3) and coatweight (-1) give negative overall responses, ash (0) gives a zero, and protein (+1), basis weight (+4) and pigment (+8) give positive overall responses. Of course, it must kept in mind when considering this representation of results that the regression analyses looked at all samples without regard to interactions such as the obvious linkage between increasing pigment, coatweight, ash and basis weight due to the use of a constant basestock, for example. In a production environment, one would expect to maintain total basis weight while substituting coating for fiber to optimize economics. It may be more logical to examine the responses grouped into different formulation systems.

Figure 4 shows the geometric mean bending resistance as a function of basis weight. Due to significant uncertainties in total basis weight, information from all coatweights for each system have been combined, with

Gaussian error propagation computations applied for both X and Y uncertainties [22]. Error bars in the graph represent 90% confidence intervals. The cubic line has been computed as a fit through the best case data point, with 100 parts of the starch/protein binder system and 100 parts pigment. This line represents what would be expected if the basis weight of the best case system were decreased to match the weight or the bending resistance of the lighter reference system, according to Eq. 2 above. From this graph, it can be seen that the best case pigmented size system would match the bending resistance of the reference system at a total basis weight 2.9 g/m^2 lower than the reference system. That best case pigmented size system also had 2 g/m^2 greater size pickup than the reference system. Thus, a 4.9 g/m^2 reduction in fiber with the best case pigmented size system might be expected to provide equal bending resistance in comparison to the reference clear starch size. Given typical relative costs of fiber versus the starch, protein and pigment sizing system, in most cases this should represent a compelling economic incentive for use of this type of system. Aside from the material costs alone, there would almost certainly also be significant cost reductions when reducing this quantity of fiber on the wet end of a paper machine.

Figure 4. Best Case Projected Fiber Reduction Based on Bending Resistance.

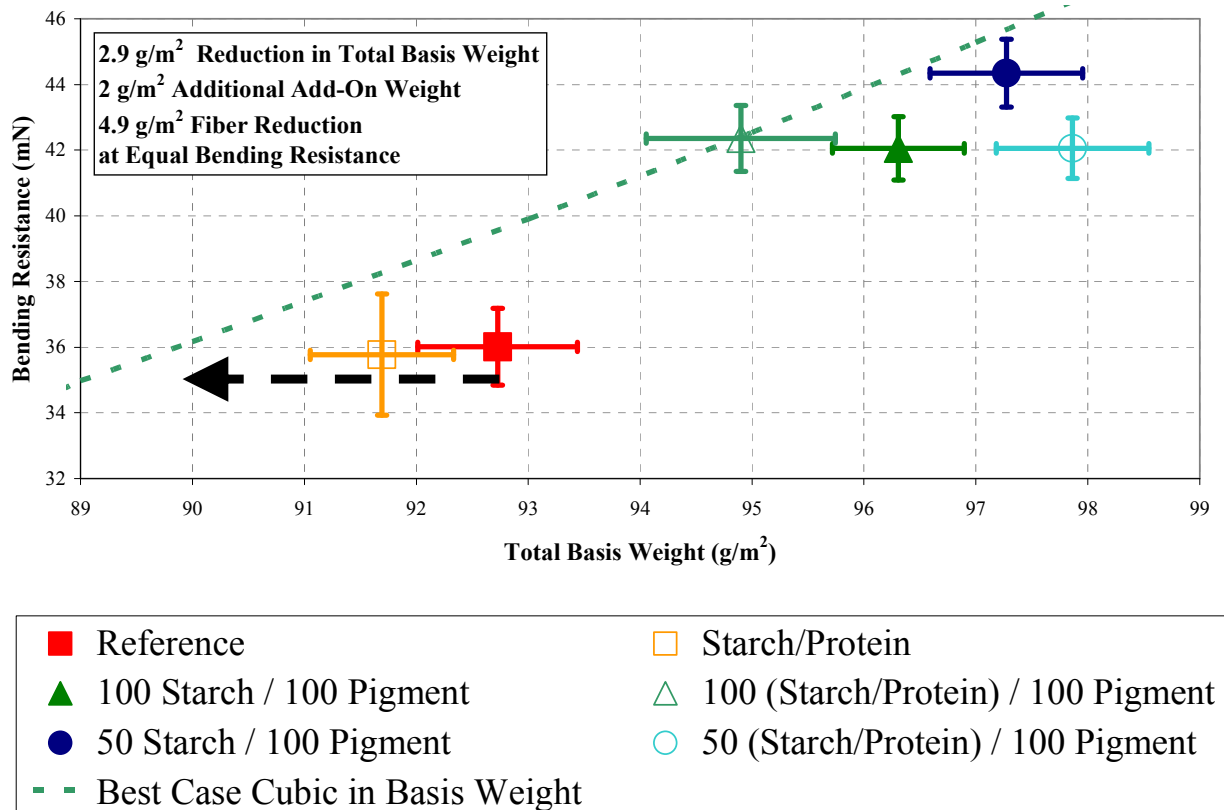


Figure 5 presents a similar average basis weight treatment of Hercules Size Test data. This graph shows that while pigmenting had little effect on the Hercules Size Test, use of protein in combination with the starch provided huge boosts to fluid holdout. A variety of other properties were also influenced by both the type of binder and the amount of coating applied. For example, Parker Print-Surf S10 Roughness in Figure 6 has very strong dependence on coatweight for the starch/protein systems, and those starch/protein systems generally produced smoother surfaces. Figure 7 shows Scott Bond vs. size press pickup. In this data, the dependence on coatweight is strong for the clear sizes, but that dependence weakens as pigment is added. Without pigment, no effect is seen from protein. However, once pigment is included, it appears that the Scott Bond internal strength decreases when protein is also included. Reduction in Scott Bond may be related to improved size holdout. Brightness mottle contrast vs. coatweight is shown in Figure 8. This also shows a dependence on coatweight that decreases with increasing pigment, but there is a clearer differentiation between the starch-only and starch + protein clear size systems. The behaviors seen in Figures 6 through 8, among other properties, lead the authors to believe that both protein and pigment in the size

formulation contribute to physical holdout of the size above the basestock fiber network, reducing penetration into that network and creating a more continuous sizing film.

Figure 5. Hercules Size Test of the Various Sizing Systems.

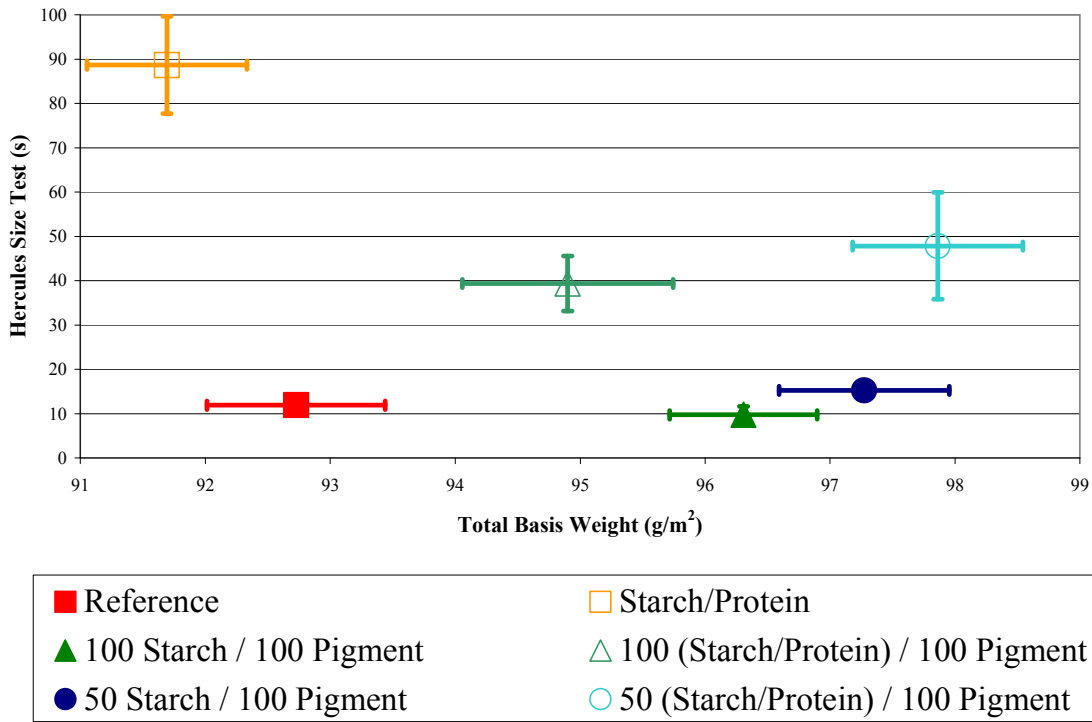


Figure 6. Parker Print-Surf Roughness Dependence on Coatweight.

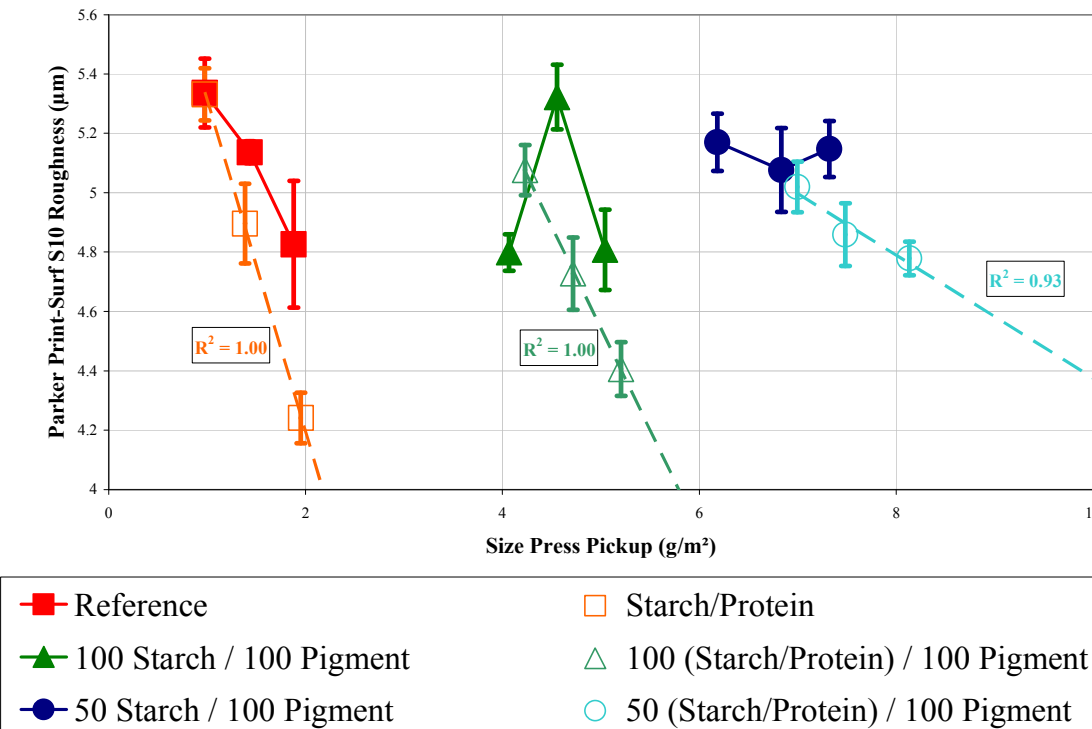


Figure 7. Scott Bond Dependence on Coatweight.

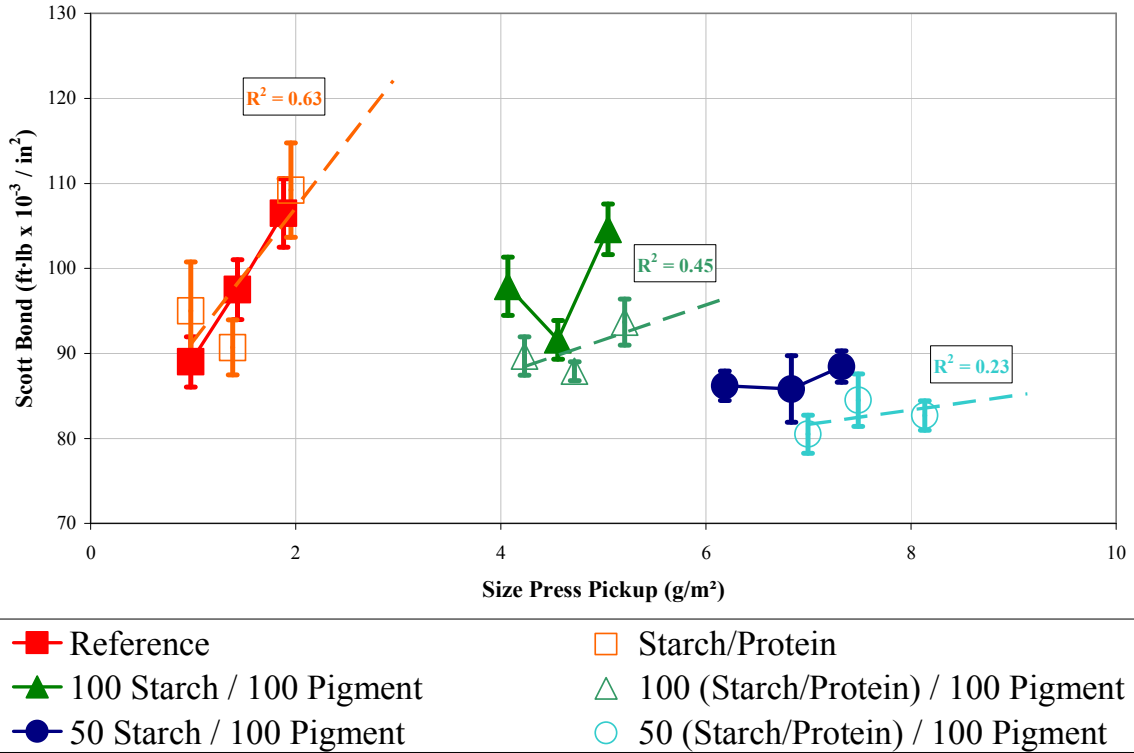
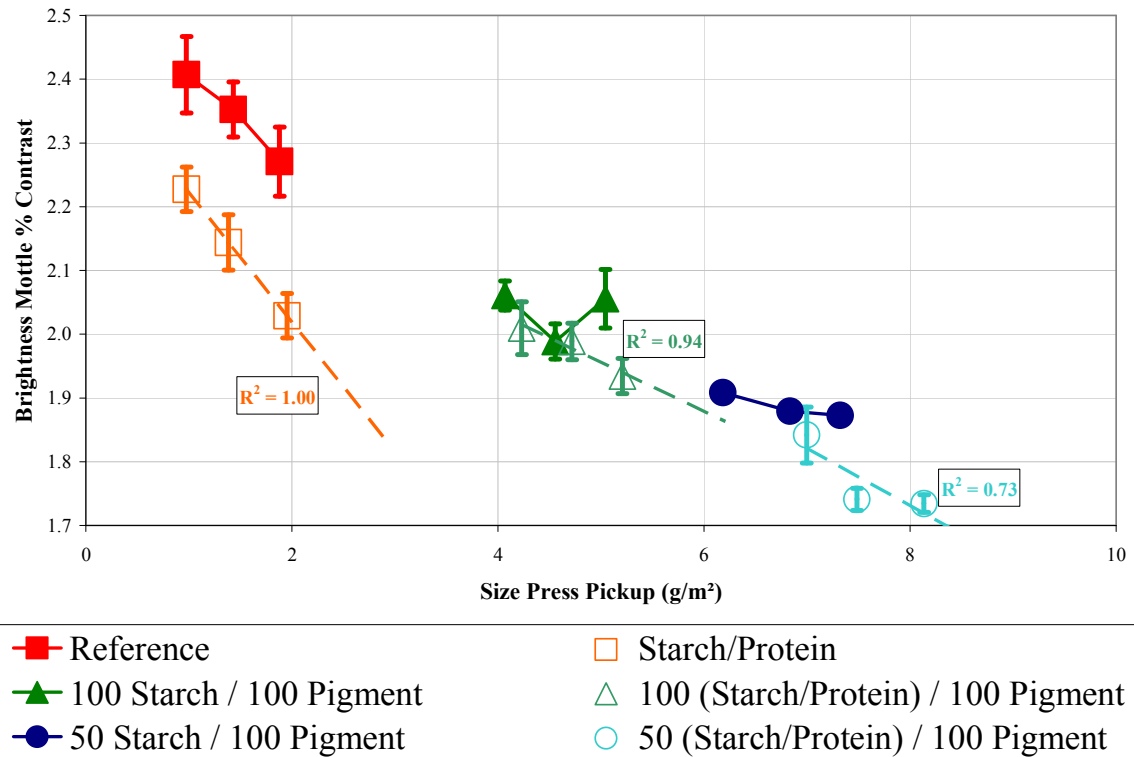
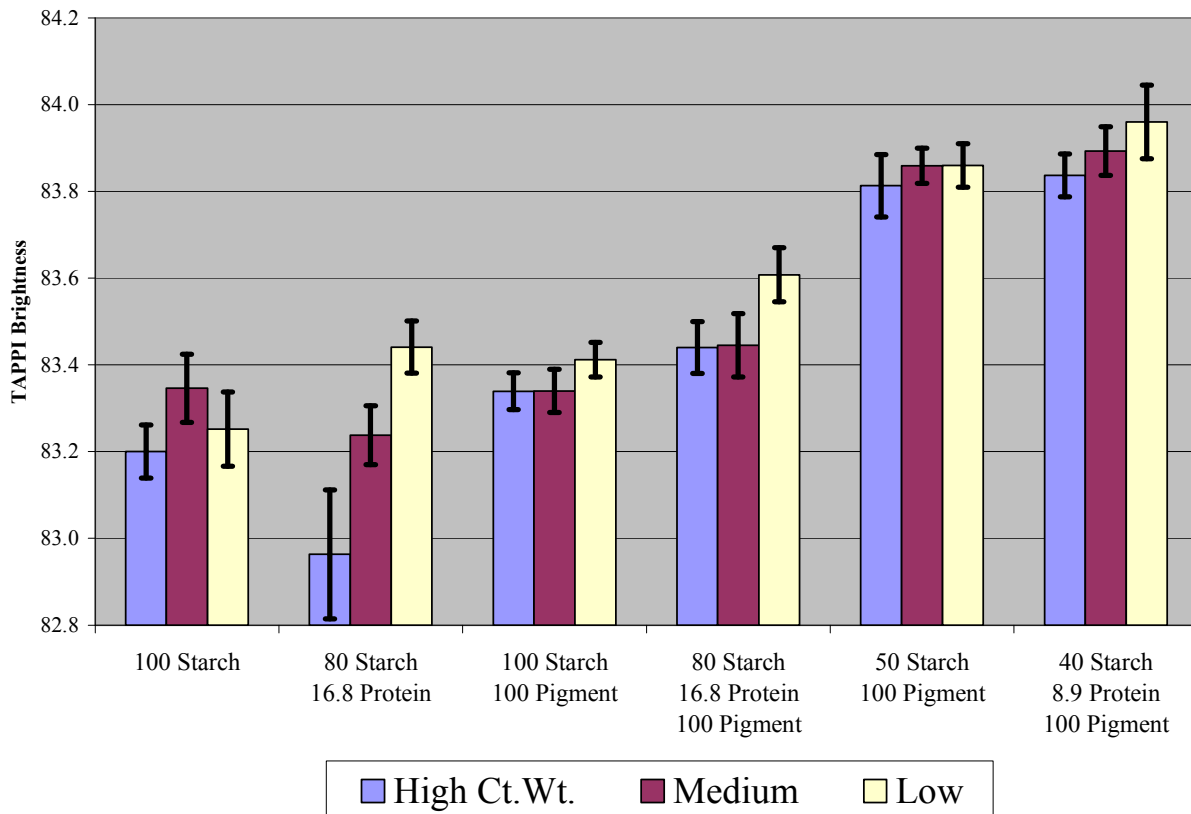


Figure 8. Brightness Mottle Contrast Dependence on Coatweight.



One optical property for which there had been considerable concern about degradation using kaolin was the brightness of the sheet. However, using a high ratio of GCC to kaolin, and high brightness kaolin, actually improved the sheet brightness. This result is illustrated in Figure 9.

Figure 9. TAPPI Brightness Response of Various Sizing Systems.



CONCLUSION

As stated earlier, a key driver for papermakers in the current economic environment is to reduce raw material costs. By replacing fiber weight by pigmented size, a significant degree of savings might be achieved. These savings would come not only through fiber reduction, but also in energy and perhaps chemical costs. By capitalizing on stiffness developments, a paper producer may be able to reduce fiber weight by between 1 and 5 percent, thereby reducing the energy demands in the dryer section. This would likely result in either an increase in productivity or a reduction in steam usage. Additionally, mills producing market pulp would increase the overall percentage of saleable fiber, whilst mills purchasing fiber on the market would lower the raw material demands on a ton/produced paper basis.

Particular take away points include:

- The data clearly demonstrates the ability to trade pigmented size for fiber
- Improved holdout related to both protein and pigment can be inferred from results of Hercules Size Test, Scott Bond, Parker Print-Surf Roughness and Brightness Mottle Contrast
 - Fluid holdout related to improved film continuity
- Advanced rheometry clearly demonstrates the existence of long range, three dimensional wet networks in blends of protein and starch
 - This and holdout signals clearly differentiate between starch-only and starch/protein binder systems

Several questions have been raised by the results presented:

- What is the mechanism of improved holdout, how might it be confirmed?
- If there is a more continuous film, will it provide improved binding of fiber and pigment for improved cleanliness at the printer?
- What benefits would this system bring to printing processes such as xerography, inkjet, offset?
- Could this type of system contribute to barrier functionality?
- Would this system perform similarly if applied using different types of applicators?
- If the entire pigment system were platy, how much more improvement would be seen?

The authors hope that the results presented and the further questions they have raised will encourage others to continue investigation of this line of research.

REFERENCES

1. "Future Requirements Of Printing Papers And Effects On The Characteristics Of Pigment Coating". Hirsch G; Reinbold I; Rohmann M, vol 35 no 3 Mar 1981 pp 108-116 ; Pira Translation no 2562
2. "Evaluation and control of coated paper stiffness," Okomori, K., Enomae, T. and Onabe, F., TAPPI 1999 Advanced Coating Fundamentals Symposium, April 29 – May 1, 1999, Toronto, Ontario, Canada.
3. "Evaluation and control of coated paper stiffness," Okomori, K., Enomae, T. and Onabe, F., Journal of Pulp and Paper Science, v 27, n 8, p 262-267, August, 2001
4. "A mechanism to explain particle size segregation and binder depletion during coating", Gagnon R E; Parish T D; Bousfield D W, Coating conference, Washington, DC, USA, 1-4 May 2000, pp 77-90, TAPPI Press.
5. "Fine tuning dynamic mechanical properties of latex and adjusting coating parameters for maximum coated paper stiffness," Jud, C., Hahn, N., and Kan, C., TAPPI - Polymers, Laminations and Coatings Conference, 431-443, 2000 TAPPI Coating Conference and Trade Fair, May 1-May 4 2000, Washington, DC , USA.
6. "Coated paper Stiffness: a practical perspective", Kim-Habermehl L H; Pollock M J; Kan C; Oates J D; Williamson G D, 2000 International printing and graphic arts conference, Savannah, GA, USA, 1-4 Oct. 2000, pp 311-318, TAPPI Press
7. "Modeling of Coating Layer Mechanical Properties", Toivakka, M. and Bousfield, D., TAPPI Advanced Coating Fundamentals Symposium, May 4 – 5, 2001, San Diego, CA, USA.
8. "Optimisation of the precoating share and binder composition of double coated woodfree papers to improve quality and reduce costs", Glittenberg D; Voigt A; Becker A; Aarnio Y, 21st PTS Coating Symposium, 16-19 Sept. 2003, 13 pp, PTS Symposium ST 301, Munich, Germany: Papiertechnische Stiftung, 2003, 456pp
9. "Mechanical properties of coated paper: Influence of coating properties and pigment blends," Morsy, F.A. and El-Sherbiny, S., Journal of Materials Science, v 39, n 24, p 7327-7332, Dec 15, 2004.
10. "Size Press Filling Boosts Ash Content, Enhances Uncoated Free-sheet Quality," Altemeier, M., Meyers, R. and Aviles, F., Pulp and Paper, v 78, n 1, p 52-54, January, 2004.
11. "Mechanical properties of coating layers," Ratto, P., Journal of Pulp and Paper Science, v 30, n 12, p 335-340, December, 2004.
12. "Nanodimensional engineering of coating to enhance the value of paper", Lyons T, Nanotechnology for papermakers, Stockholm, Sweden, 29 Nov. 2004, 19pp, UK: Pira International.
13. "Optimization of latex binder properties for premetering size press runnability, paper gloss development and Stiffness", Stollmaier F; Lohmuller G; Pykalainen N, 2004 Coating and Graphic Arts Conference and Exhibit, Baltimore, MD, USA, 16-19 May 2004, 14pp Atlanta, GA, USA: TAPPI Press, 2004
14. "Novel silicate "fibrous fillers" and their application in paper," Mathur, Vijay K., p 83-139, 2004, 2004 TAPPI Paper Summit - Spring Technical and International Environmental Conference.
15. "Impregnating paper with fillers. Advantages of bringing additional pigments through the surface into the paper," Gisella, Uwe and Laufmann, Max, Papier Aus Osterreich, n 5, p 26-27, May, 2005.
16. "Surface sizing additives", Sajbel J, Sizing of paper, edited by J M Guess and F M Rodriguez, chapter 15, pp 287-299, 3rd edition, TAPPI Press, 2005, 363pp.
17. "The influence of pigment particle shape on the in-plane tensile strength properties of kaolin-based coating layers," Husband, J.C., Preston, J.S., Gate, L.F., Storer, A. and Creaton, P., 2006 TAPPI Advanced Coating Fundamentals Symposium, v 2006, p 341-353.

18. "The influence of pigment particle shape on the in-plane tensile strength properties of kaolin-based coating layers," Husband, J.C., Preston, J.S., Gate, L.F., Storer, A. and Creaton, P., TAPPI Journal, v 6, n12, December, 2006.
19. "A Study Of In-Plane And Z-Direction Strength Of Coating Layers With Varying Latex Content," Husband, J.C., Preston, J.S., Gate, L.F., Storer, A.† and Creaton, P., TAPPI Journal, accepted for publication in early 2007.
20. "Analysis of the effect of porosity and pigment shape on the stiffness of coating layers," Lepoutre, P. and Rigdahl, M., Journal Material Science 24:2971-2974 (1989).
21. "Apparatus and method for measuring the average aspect ratio of non-spherical particles in a suspension," US Patent 5,576,617, November 19, 1996.
22. "Introduction to the theory of error," Beers, Y., Addison-Wesley Pub. Co., Cambridge, MA, 1953.

APPENDIX

Materials Identification

GCC1 – IMERYS Carbital 90

GCC2 – IMERYS Carbital 60

KaolinA – IMERYS Contour 1500

KaolinB – IMERYS Contour Xtreme

Starch – A.E. Staley Ethylex 2040

Protein – DuPont Soy Polymers Pro-Cote 4200

Coated Paper Property Measurement Results

Condition ID	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Coating ID	Reference	Reference	Reference	One	One	One	Two	Two	Two	Three	Three	Three	Four	Four	Four	Five	Five	Five	
Total Basis Weight (g/m ²)	Mean	92.3	93.3	92.6	92.9	90.9	91.2	97.6	96.2	95.2	96.4	94.5	93.8	98.9	96.6	96.4	97.5	98.6	97.5
	90% Conf.	0.7	1.3	1.6	1.3	0.3	1.4	1.3	0.2	1.2	1.6	1.6	1.2	0.3	1.2	1.6	1.6	0.6	1.1
Coatweight (g/m ²)	Mean	1.9	1.4	1.0	2.0	1.4	1.0	5.0	4.6	4.1	5.2	4.7	4.2	7.3	6.8	6.2	8.1	7.5	7.0
450° C Ash	Mean	16.4	16.5	16.8	17.2	16.3	16.7	19.7	19.2	19.2	19.5	19.6	19.5	21.3	21.2	20.8	21.0	20.6	21.4
900° C Ash	Mean	10.0	10.1	10.2	10.3	10.1	10.2	12.3	11.9	12.1	12.4	12.3	12.2	13.4	13.3	13.2	13.9	13.6	13.7
% CaCO ₂	Mean	14.6	14.7	15.0	15.6	14.3	14.8	16.7	16.7	16.2	16.3	16.5	16.6	17.8	17.9	17.2	16.3	15.9	17.4
% Other	Mean	1.8	1.8	1.8	1.6	2.0	1.9	3.0	2.5	3.0	3.3	3.1	2.8	3.5	3.3	3.5	4.7	4.7	4.0
Geometric Mean Bending Resistance (mN)	Mean	34.3	35.8	38.0	31.2	35.6	40.5	43.2	38.9	44.0	43.3	40.9	42.8	45.5	45.4	42.2	41.2	40.9	44.0
	90% Conf.	1.8	2.0	2.2	2.3	0.9	5.0	1.8	0.5	2.3	1.4	1.7	2.1	1.6	1.8	2.0	2.0	1.5	1.1
Burst (psi)	Mean	38.4	38.5	37.1	35.1	32.3	33.9	38.7	38.0	38.5	36.0	34.3	34.9	40.3	36.7	37.4	35.8	34.5	34.4
	90% Conf.	1.7	0.6	1.5	2.0	1.2	1.4	1.1	2.1	1.1	1.6	1.4	1.6	1.2	1.8	0.7	1.0	1.2	0.9
Scott Bond	Mean	107	98	89	109	91	95	105	92	98	94	88	90	88	86	86	83	85	81
	90% Conf.	4	4	3	6	3	6	3	2	3	3	1	2	2	2	4	2	3	2
IGT Dry Pick (vvp)	Mean	114	116	119	110	113	114	143	148	146	125	128	122	132	133	130	116	111	112
	90% Conf.	3	4	3	5	6	8	5	7	9	4	7	6	5	3	8	4	7	4
Linting	Mean	0.021	0.022	0.010	0.021	0.021	0.022	0.008	0.018	0.017	0.017	0.029	0.015	0.017	0.022	0.010	0.030	0.024	0.024
	90% Conf.	0.026	0.065	0.014	0.035	0.046	0.023	0.032	0.023	0.023	0.024	0.025	0.031	0.027	0.020	0.018	0.037	0.015	0.026
Caliper (um)	Mean	111.0	111.3	113.1	106.8	111.9	115.2	113.3	110.9	113.2	110.5	110.2	112.6	114.2	113.4	112.3	109.5	111.5	113.6
	90% Conf.	3.1	1.3	1.6	1.0	0.8	0.9	1.6	1.6	2.0	1.4	1.6	1.0	1.3	1.4	1.3	1.0	2.4	1.3
Bulk (um/(g·m ²))	Mean	1.20	1.19	1.22	1.15	1.23	1.26	1.16	1.15	1.19	1.15	1.17	1.20	1.16	1.17	1.16	1.12	1.13	1.17
	90% Conf.	0.04	0.02	0.03	0.02	0.01	0.02	0.02	0.02	0.03	0.02	0.03	0.02	0.01	0.02	0.02	0.02	0.03	0.02
Low Pressure Gurley Air Permeability (s/25 cc)	Mean	27.1	26.4	25.4	33.0	28.9	26.7	96.1	105.0	78.6	80.9	70.6	65.5	140.4	131.3	127.3	195.9	168.2	162.3
	90% Conf.	2.4	1.6	0.8	2.2	3.0	2.5	4.3	11.4	2.4	9.3	7.8	6.4	10.6	7.8	10.5	7.2	14.4	17.7
PPS S10 Roughness (um)	Mean	4.83	5.14	5.34	4.24	4.90	5.33	4.81	5.32	4.80	4.41	4.73	5.08	5.15	5.08	5.17	4.78	4.86	5.02
	90% Conf.	0.21	0.04	0.12	0.09	0.13	0.09	0.14	0.11	0.06	0.09	0.12	0.08	0.09	0.14	0.10	0.06	0.11	0.09
Sheffield Roughness	Mean	105	106	119	79	86	107	94	82	101	82	89	91	86	98	89	77	82	94
	90% Conf.	13	4	5	2	3	5	7	3	10	4	9	5	2	8	5	2	2	6
Static COF	Mean	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.5	0.5	0.5
	90% Conf.	0.0	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Kinetic COF	Mean	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	90% Conf.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Brightness Mottle % Contrast	Mean	2.27	2.35	2.41	2.03	2.14	2.23	2.06	1.99	2.06	1.93	1.99	2.01	1.87	1.88	1.91	1.73	1.74	1.84
	90% Conf.	0.05	0.04	0.06	0.03	0.04	0.03	0.05	0.03	0.02	0.03	0.03	0.04	0.03	0.01	0.01	0.01	0.02	0.04
Paprican Microscanner Formation	Mean	78.0	71.0	72.0	84.8	74.0	74.4	78.4	79.8	76.2	79.4	76.8	74.8	79.6	78.6	79.6	86.0	85.6	81.2
	90% Conf.	3.2	5.6	4.3	5.4	3.2	3.4	5.9	3.2	3.6	4.5	4.1	5.1	4.4	3.5	2.2	3.3	4.2	3.5
Dry Prubau Heatset Magenta Print Density	Mean	1.10	1.07	1.08	1.12	1.09	1.05	1.07	1.08	1.05	1.07	1.06	1.08	1.09	1.06	1.08	1.09	1.11	1.09
	90% Conf.	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01
Ink Setoff	Mean	0.80	0.81	0.86	0.80	0.80	0.82	0.80	0.83	0.82	0.80	0.82	0.82	0.84	0.81	0.83	0.81	0.81	0.81
	90% Conf.	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02
Croda Redwipe % Contrast	Mean	13.3	13.2	13.4	12.8	13.2	13.8	14.9	14.6	14.0	14.2	14.3	14.5	16.4	16.0	15.2	16.1	15.5	15.7
	90% Conf.	0.7	0.7	0.2	0.2	0.4	0.3	0.5	0.4	0.3	0.5	0.3	0.2	0.8	0.2	0.6	0.2	0.6	0.6
Croda Redwipe 8 bit Graytone	Mean	65	64	62	70	66	63	81	81	78	77	76	77	86	84	82	87	83	82
	90% Conf.	2	2	1	2	2	1	3	1	2	1	2	2	3	2	2	2	1	3
Hercules Size Test (s)	Average	11.6	11.8	12.4	93.3	84.6	88.0	10.7	9.1	9.5	37.3	40.4	40.4	16.6	15.6	13.6	47.5	51.0	45.0
	90% Conf.	0.8	0.4	0.3	7.0	6.1	5.9	1.2	1.2	0.8	4.0	2.8	3.9	1.2	0.8	0.4	5.3	10.4	2.9
Brightness - TAPPI	Mean	83.2	83.3	83.3	83.0	83.2	83.4	83.3	83.4	83.4	83.4	83.4	83.6	83.8	83.9	83.9	83.8	83.9	84.0
	90% Conf.	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.1	0.1
Opacity - TAPPI	Mean	94.9	94.9	95.1	94.5	94.8	94.8	95.1	95.0	94.9	95.2	95.0	95.2	95.3	95.4	95.0	95.3	95.3	95.2
	90% Conf.	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.1
Hunter b - TAPPI	Mean	-0.9	-0.8	-0.8	-0.5	-0.6	-0.6	-0.6	-0.6	-0.6	-0.5	-0.5	-0.5	-0.6	-0.6	-0.6	-0.5	-0.5	-0.4
	90% Conf.	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fluorescence - TAPPI	Mean	1.1	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9	1.0
	90% Conf.	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Whiteness - TAPPI	Mean	85.7	85.6	85.5	84.0	84.8	85.0	84.9	84.9	84.9	84.6	84.6	84.9	85.3	85.3	85.3	84.8	84.9	84.9
	90% Conf.	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sheet Gloss (75)	Mean	10.5	9.9	9.9	11.5	10.8	9.7	8.8	10.0	8.9	9.4	9.6	9.1	7.6	7.5	8.3	8.5	8.5	8.0
	90% Conf.	0.4	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.1	0.2	0.2	0.2	0.2	0.2	0.1	0.2
Print Gloss (75)	Mean	18.5	17.7	16.6	19.7	18.8	16.1	20.0	20.3	18.1	18.1	17.4	19.2	20.1	19.6	19.9	21.7	22.1	20.7
	90% Conf.	0.6	0.5	0.6	0.7	0.5	0.3	0.6	0.2	0.5	0.3	0.4	0.4	0.4	0.6	0.4	0.7	0.3	0.6
Delta Gloss	Mean	8.0	7.8	6.7	8.2	8.0	6.4	11.2	10.3	9.2	8.7	7.8	10.2	12.5	12.1	11.6	13.2	13.6	12.6
	90% Conf.	0.7	0.5	0.6	0.7	0.6	0.4	0.6	0.3	0.5	0.4	0.4	0.5	0.5	0.6	0.5	0.8	0.4	0.6
F8 Scatter	Mean	658.2	650.2	700.0	661.1	703.7	702.6	667.4	674.0	683.3	674.2	711.0	707.4	683.7	705.9	706.5	720.5	721.9	751.5
F8 Absorption	Mean	11.2	10.8																