The use of hollow sphere pigments as strength additives in paper and paperboard coatings—Part 2: Optimization in paperboard formulations for opacity and strength

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ABSTRACT: This report aims to summarize the efforts in testing the properties of coatings for paperboard utilizing hollow sphere pigments (HSPs). HSPs are known to effectively scatter light and replace titanium dioxide (TiO_2) in architectural coating formulations. The effect of the particle size and void fraction was evaluated, along with many coating parameters, including level of addition, binder chemistry, and blends of two HSPs.

The small HSPs that have optimized voids for scattering light showed equivalent strength to the TiO_2-containing control. The strength data was surprising, particularly the improvement in strength for coatings containing large particle size HSPs. Because of this increase in strength, four parts of binder could be removed, which allowed for higher brightness while not compromising other properties, including hot melt glueability. These trends held true using different binder chemistries (styrene acrylic, vinyl acrylic, and styrene butadiene). Upon refining the formulations further, blends of two HSPs showed further benefit.

Application: This work shows that replacement of TiO_2 with hollow sphere pigments can improve the balance of physical properties of paperboard coatings. By utilizing large particle size HSPs, one can replace TiO_2 and reduce binder levels while maintaining brightness, strength, and other critical properties.

Paper and paperboard coatings impart improved qualities to the substrate, including smoothness, brightness, surface gloss, printability, ink/water absorbency, etc. The majority of the components in paperboard coatings are clays or calcium carbonate fillers, which form the supporting architecture of the coating layer. Binders, both synthesized polymeric particles and natural starch, are used to bind neighboring fillers in a matrix, playing a key role in determining the coating performance. Titanium dioxide (TiO_2) particles are also included for recycled and unbleached kraft paperboard coatings to add brightness (and opacity) that hides the dark substrate. Paperboard coatings normally feature high amounts of pigment volume concentration (PVC), and in most cases, these coatings are formulated with a PVC higher than the critical PVC (CPVC). Formulations beyond CPVC generally result in air voids in the dry coating films that contribute to the brightness and also affect the printability, water/ink absorbency, and pick strength.

In architectural paints, hollow sphere pigments (HSPs; also called opaque polymers) are widely used for their ability to scatter light [1-4]. The HSPs also more effectively space TiO_2 without affecting the overall performance, so they are highly effective when blended with TiO_2. In paper coatings, HSPs not only bring opacity but also excellent gloss, and the choice of HSP type is critical. Larger particle size HSPs (~1 µm) are used in coated paper formulations at very low loading levels (2 wt%–6 wt%) for their significant impact on gloss and also provide benefits of improved brightness and printability. For paperboard applications, we are less interested in these properties and want to focus on increasing the scattering efficiency of the particle to maximize the opacity. Incorporation of TiO_2 is the predominant way to improve opacity, and this work focuses on replacing TiO_2 with HSPs. It is well known that the HSP void size influences the scattering efficiency of the particle. The void size is typically optimized to be ~300 nm [5], but the high PVC paperboard coatings also have scattering sites from the interstitial air voids that impart opacity. Optimizing the size of those interstitial voids with the scattering from the HSP is the goal of this work. This report will review testing that was conducted to evaluate the impact of HSP size and usage level on overall paperboard coating performance.

EXPERIMENTAL PROCEDURES

Formulation properties

Formulation samples were prepared in a laboratory using a benchtop mixer and adjusted to pH 8.0–8.5 with dilute sodium hydroxide. Rheology modifier was added to adjust the Brookfield viscosity to ~80 cP at 100 rpm. The Brookfield viscosity was measured using Model DV II+ Brookfield viscometer (Brookfield Engineering Laboratories; Middleboro, MA, USA) at 100 rpm. Hercules viscosity was measured using Hercules high shear viscometer LV-10, and two runs were taken for each sample.

Coating preparation

Paperboard was cut into approximately a 12 in. x 12 in. size for coating application. Kraft paperboard (61.2 lb/1000 ft^2) was coated for brightness measurements, and solid bleached sulfate (SBS) paperboard (42.8 lb/1000 ft^2) was coated for all other analyses. Drawdowns were made by different wire rods at various speeds to achieve desired coat weight using a K control coater from RK PrintCoat (Litlington, UK). All drawdowns were applied in the machine direction (MD). After being coated, the boards were dried for 2 min at 80°C. After conditioning for at least 2 h at 72°C/50% relative humidity (RH), the coated boards were then calendered under heat and pressure using the Beloit Wheeler Model 754 gloss calender stack at 165°F, 600 psi, and 75 rpm.

Coat weight measurement

The coat weight measurement was carried out using a 2-1/8 in. x 3-3/8 in. rectangle punch. Six 2-1/8 in. x 3-3/8 in. rectangles were punched from the paperboard. The rectangles were then weighed and that number was then divided by six. This value was then multiplied by the factor (44.265 for lb/1000 ft^2) to get the basis weight of the substrate. The previous steps were then repeated for the coated substrates. The coat weight was obtained by taking the difference between the basis weight and the coated substrate weight. Coat weights of ~3.5 lb/1000 ft^2 were targeted for SBS and kraft paperboards.

Gloss measurement

Gloss was measured using Technidyne Test/Plus Gloss meter (Technidyne; New Albany, IN, USA), which measures 75° gloss. There were 10 data points taken for each sample to obtain the average gloss value.

Brightness measurement

Coating brightness was measured using a Technidyne Test/Plus TAPPI Brightness meter. There were 10 data points taken for each sample to obtain the average brightness value.

IGT dry pick measurement

IGT dry pick measurement was carried out using IGT AIC 2-5 unit (IGT Testing Systems; Almere, The Netherlands). Coated paperboard samples were cut into 1.5 in. x 12 in. size and mounted onto the equipment using a WestVaco wheel. IGT was measured according to the IGT WestVaco pick test W38, and three readings were taken to get an averaged value of IGT pick strength. IGT measurements were performed in the MD and medium viscosity ink from IGT (IGT Pick Test Ink Nr. 2, medium tack, 404.800.002) was typically used for measurements.

Hot melt glueability test

Coated paperboard was cut into 1.5-in. MD x 6-in. cross direction (CD), and a continuous bead of hot melt glue was applied approximately 1/8 in. wide by 5 in. long to the coated side of one sample. The glued sample was then immediately matched to the coated side of the other sample. A 1.5 lb weight (3 in. x 7 in. x 0.25 in.) was then placed on the glued sample for 30 s. Afterwards, the weight was then removed and the samples were allowed to cool for an additional 30 min. After the sample was set for at least 30 min, the matched samples were pulled apart. The amount of fiber that was attached to the glue was then recorded in percentage. The higher amount of fibers that were stuck on glue (% of fiber tear) is indicative of better performance.

RESULTS AND DISCUSSION

Part 1: Impact of particle size and void fraction

The first set of experiments to replace TiO_2 with HSP was conducted using a formulation containing clay and TiO_2, as shown in **Table I**. A range of HSPs was evaluated at 50% and 100% replacement levels for TiO_2. In addition to opacity changes, the rheological properties and strength of the coatings were measured. Six HSPs were studied to determine the impact of particle size and void fraction. Four different particle sizes were used (450 nm, 1 µm, 1.3 µm, and 1.5 µm). The impact of void fraction was determined using particles at the 450-nm size. HSPs provide an ideal system through which one can examine the effect of pigment size and particle packing within a coating due to their unimodal and tunable particle sizes (**Table II**). Particle sizes were

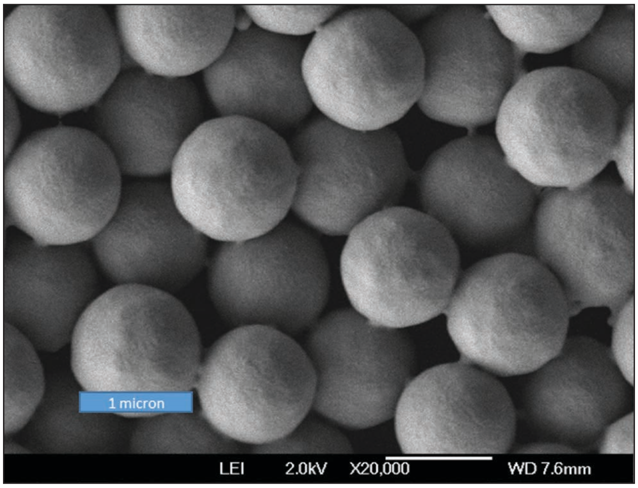
	Control TiO_2 Parts	50/50 TiO_2/HSP Parts	100 HSP Parts
#1 Clay	85.0	85.0	85.0
TiO_2	15.0	7.5	-
HSP	-	7.5	15.0
Vinyl acrylic latex	20.0	20.0	20.0
Rheology modifier	0.3	0.3	0.3
Total Parts	**120.3**	**120.3**	**120.3**

TiO_2 = titanium dioxide; HSP = hollow sphere pigment.

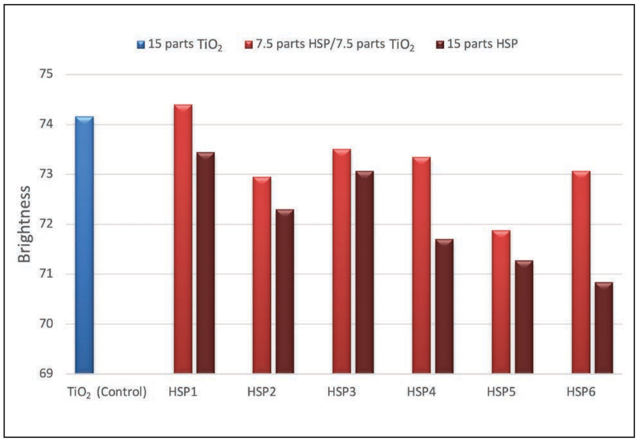
I. Coating formulations.

	Particle Size, Nm	Void Fraction, %	Solids, %
HSP1	450	45	30.0
HSP2	450	38	35.0
HSP3	450	53	28.5
HSP4	1000	55	26.5
HSP5	1300	53	26.5
HSP6	1500	63	20.0

II. Hollow sphere pigment (HSP) properties.



1. Surface scanning electron microscope (SEM) image of the HSP4 hollow sphere pigment (HSP).



2. Effect of brightness on HSP type and replacement level (TiO_2 = titanium dioxide).

measured experimentally via scanning electron microscope (SEM), and void fractions were measured experimentally (**Fig. 1**) [6].

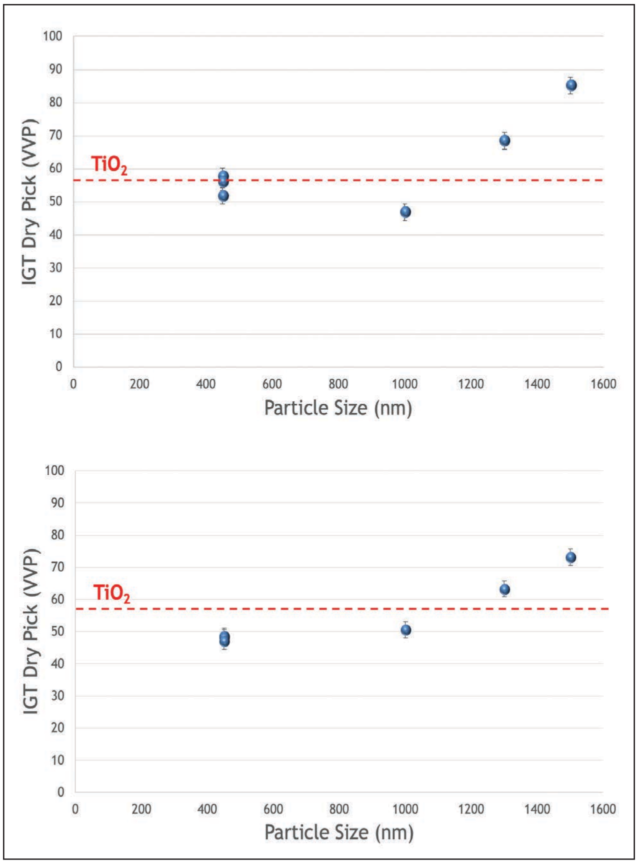
The wet formulation properties were similar to the control. There was a bump in the Hercules high shear viscosities when using any of the HSPs, but all values were close to the control and well within runnable ranges. The gloss values increased significantly with HSP content from 35 for the control (no HSP) to ~50 at 100% replacement of TiO_2 for HSP (**Table III**). HSP5 was designed to generate the highest gloss in coated paper formulations, and here they also had the highest gloss, with a 3-point margin above the next HSP. Since the goal was to replace TiO_2 with HSP, the brightness of the board was critical.

Largely, the brightness decreased as HSP was substituted for TiO_2 (**Fig. 2**). At 50% replacement, the HSPs were

Pigment Information	Parts	pH	AA-GWR	Brightness	Gloss	PPS	Wet Rub	Brookfield Viscosity @ 100 rpm	IGT-VVP (Continuous)	Deltack Slope	Deltack Passes-to-Failure	Hot Melt Glueability
TiO_2	15.0	8.4	246	74.2	34.1	2.9	96	81.6	56	0.81	7.0	100%
HSP1	7.5	8.3	264	74.4	42.0	2.5	97	88.8	52	1.04	5.0	100%
	15.0	8.4	297	73.4	49.8	2.3	98	81.6	48	1.82	4.0	100%
HSP2	7.5	8.4	253	72.9	39.4	2.7	97	67.6	58	0.94	6.5	100%
	15.0	8.4	254	72.3	43.7	2.5	96	93.6	48	1.22	4.0	100%
HSP3	7.5	8.5	239	73.5	42.1	2.9	95	74.4	56	1.21	6.0	100%
	15.0	8.4	230	73.0	50.4	2.9	98	86.4	47	1.28	3.5	100%
HSP4	7.5	8.4	234	73.3	42.8	2.6	97	76.8	47	1.01	6.0	100%
	15.0	8.5	223	71.7	50.2	2.3	99	69.6	51	0.81	6.5	100%
HSP5	7.5	8.5	256	71.8	41.9	2.5	93	78.0	68	0.65	8.0	100%
	15.0	8.4	258	71.2	53.0	2.3	99	71.2	63	0.58	7.0	100%
HSP6	7.5	8.4	257	73.0	40.3	2.4	96	72.0	85	0.68	14.0	100%
	15.0	8.4	259	70.8	50.3	2.2	97	66.0	73	0.73	9.0	100%

TiO_2 = titanium dioxide; HSP = hollow sphere pigment; AA-GWR = water retention meter; PPS = Parker Print Surf; VVP = viscosity-velocity product.

III. Wet formulation and coating application properties as a function of HSP incorporation.



3. IGT dry pick as a function of particle size. Top image shows 50% TiO_2 replacement, and bottom image shows 100% TiO_2 replacement (VVP = viscosity-velocity product).

ranked as follows in terms of highest brightness first: HSP1 > HSP3 = HSP4 > HSP6 > HSP2 > HSP5. The trend does not clearly follow void size or particle size. However, since the particles are formulated at the same dry weight percent, there are very different numbers of particles for each HSP given that they have varied particle sizes and void fractions.

The strength properties were particularly interesting. The IGT dry pick (**Fig. 3**) and Deltack passes-to-failure were significantly higher for the largest particle size, HSP6, and modestly higher for second largest, HSP5. This trend held true at both the 50% and 100% TiO_2 replacement levels. All three HSPs with a 450-nm particle size had equivalent strength to the TiO_2-containing control and to each other; of which the latter was a bit surprising. Given that the HSPs were charged at the same weight percent and each was a different void fraction, the total number of particles in the formulation differed. Since our understanding of strength is related to contact points between particles, the expectation was that the strength would decrease with higher void fraction HSPs (more particles). With that in mind, there must be a different reason for the strength changes with particle size and the lack of strength change with number of particles.

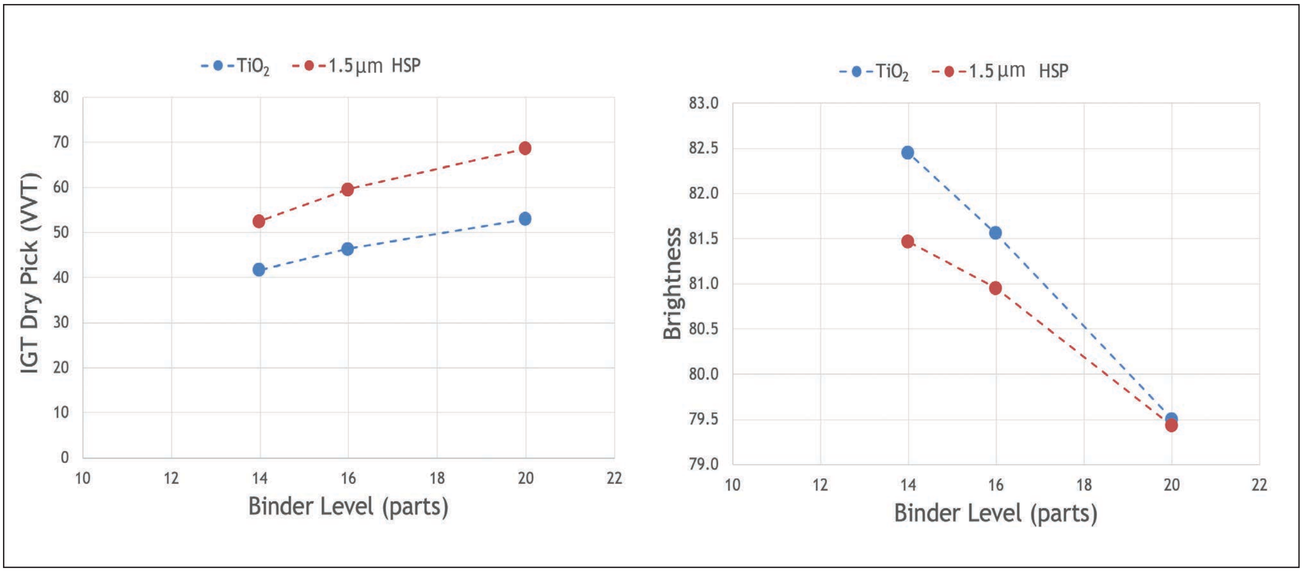
Binary blends of particles maximize the random close packing of spheres and improve the mechanical properties of coatings. Improved strength was demonstrated when thermal paper formulations were optimized for maximum packing density using binary HSP blends and identifying the correct HSP particle size to blend with calcined clay in thermal paper basecoats [7]. The formulations for the board coatings are more complex in the number of components and the understanding of the clay composition, particularly the range of particle sizes. With that in mind, additional experiments were conducted to elucidate the effect of larger particle size HSPs on strength and determine whether a larger particle size HSP provides a better balance of strength and brightness.

Part 2: A study of binder level requirements with various levels of HSP

There has been a great deal of interest over the last 15 years in decreasing the binder level for cost reduction [8,9]. Overall, latex is the most expensive component in a paper coating formulation and it has already been reduced significantly, but there is still interest in further decreasing the binder levels for cost optimization. High strength binders across a range of chemistries have been developed to reduce binder level. The next series of tests were designed to understand if HSPs could be added for opacity and allow for lower binder usage. Using the same formulation as previously described, coatings were formulated with either TiO_2 or HSP6 (largest particle size) at 14, 16, and 20 parts vinyl acrylic binder. From the graphs in **Fig. 4**, the IGT dry pick strength decreased with binder level for both series, and the strength of the coating with TiO_2 at 20 parts binder was equivalent to the HSP6-containing coating at 14 parts binder. By reducing the binder level by 6 parts, the brightness increased from 79.5 for TiO_2 to 81.5 for HSP6. The hot melt glueability showed 100% fiber tear for the TiO_2-based coatings at only 20 parts binder, while the HSP6 coatings showed fiber tear at 16 and 20 parts. Even one point in brightness change is significant, and along with the substantial binder reduction, the coatings containing HSP6 have improved optical and strength properties.

To further show that the larger HSPs were improving the strength, a master batch of the clay formulation in Table I was prepared and TiO_2, HSP1 (450 nm), or HSP6 (1.5 μm) were added to the master batch separately at two levels (**Table IV**). The addition of any pigment led to increased brightness, with TiO_2 having the highest brightness and HSP6 the lowest. The addition of HSP6 led to improved IGT dry pick and Deltack passes, while both TiO_2 and HSP1 showed the expected decrease in strength because the overall binder content reduced as pigment was added (**Fig. 5**). This experiment is further proof that packing is playing an essential role in the mechanical performance of the coating.

Our understanding of strength, and the model by which we predict it, is based on the number of pigment

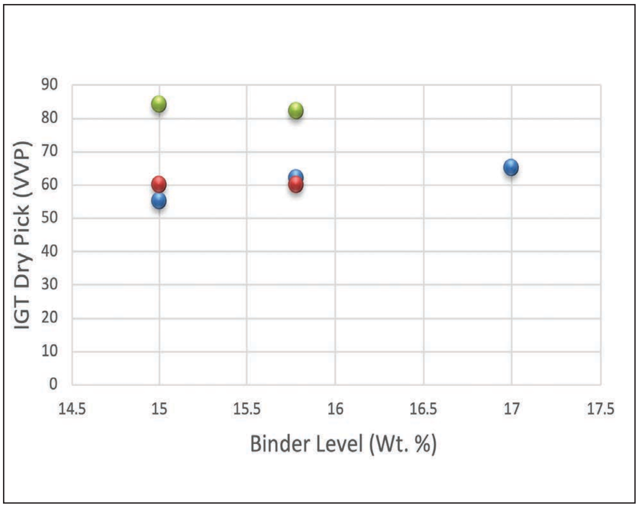


4. Effect of binder level on IGT pick strength and brightness (blue = TiO_2; red = HSP6).

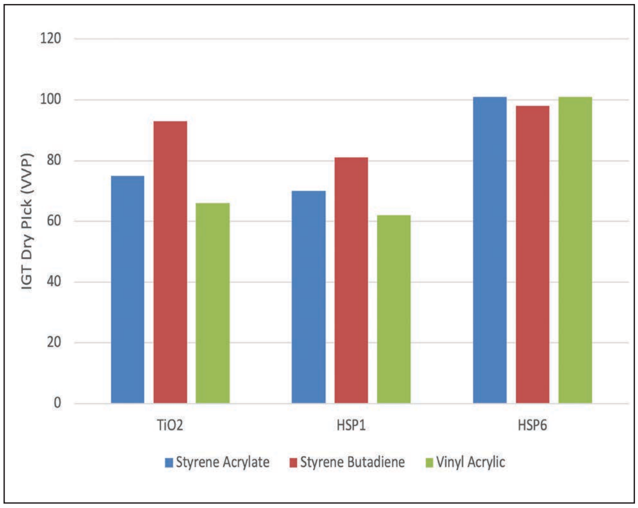
Master Batch with Added Pigment	1	2	3	4	5	6	7
	Parts	Parts	Parts	Parts	Parts	Parts	Parts
#1 clay	85.0	85.0	85.0	85.0	85.0	79.6	74.9
TiO_2	15.0	15.0	15.0	15.0	15.0	20.4	25.1
HSP6		6.7	13.5				
HSP1				6.7	13.5		
Vinyl acrylic latex	20.0	20.0	20.0	20.0	20.0	18.7	17.6
Total Parts	**120.0**	**126.7**	**133.5**	**126.7**	**133.5**	**118.7**	**117.6**
	Weight %	**Weight %**	**Weight %**	**Weight %**	**Weight %**	**Weight %**	**Weight %**
#1 clay	70.8	67.1	63.7	67.1	63.7	67.1	63.7
TiO_2	12.5	11.8	11.2	11.8	11.2	17.2	21.3
HSP6		5.3	10.1				
HSP1				5.3	10.1		
Vinyl acrylic latex	16.7	15.8	15.0	15.8	15.0	15.8	15.0
Total	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**
Coat weight (unbleached kraft softwood top, SBS bottom)	3.76	3.41	3.63	3.22	3.67	3.24	3.77
	3.27	3.66	3.00	3.75	3.46	3.64	3.21
Gloss (on SBS)	37.8	51.8	57.7	48.6	54.3	38.6	40.3
PPS (on SBS)	2.36	2.07	1.99	2.32	1.98	2.58	2.53
Brightness (on kraft)	74.2	75.0	78.7	78.3	80.0	78.2	81.4
Hot melt glueability, %	100	100	88	80	50	82	44
IGT dry pick strength, VVP	65	82	84	60	60	62	55

TiO_2 = titanium dioxide; HSP = hollow sphere pigment; SBS = solid bleached sulfate; PPS = Parker Print Surf; VVP = viscosity-velocity product.

IV. Formulation and applications testing for master batch with added pigment.



5. Effect of pigment type and binder level on IGT dry pick strength (blue = TiO_2; red = 450 nm HSP1; green = 1.5 µm HSP6)



6. Impact of binder and HSP type on IGT dry pick strength.

particles relative to binder particles. In this case, HSP6 particles are added to a set ratio of pigment-to-binder particles, and yet the strength improves. Another potential reason for the improved IGT dry pick and Deltack performance is that the HSP particles may be sealing the surface of the coating to decrease the absorbance of ink during the print tests. The HSP6 has the lowest Deltack slope, which is consistent with this hypothesis. However, the glueability data contradicts this hypothesis. Consistent with the data mentioned previously, the hot melt glueability showed 100% fiber tear for the control sample using the master batch, as well as the two samples with added HSP6, but < 100% fiber tear for the samples with added TiO_2 and HSP1.

Part 3: An evaluation of binder type and blends of HSP particles

The impact of binder chemistry was tested using a styrene acrylic binder, a styrene butadiene binder, and a vinyl acrylic binder. For each binder class, the clay formulation from Table I was used, and the TiO_2 content was replaced at 50% and 100% with HSP1 or HSP6. Although the binders showed different IGT pick strength due to their chemistry, the trends in HSP replacement were consistent across the chemistries and with the previous data. Incorporating the largest HSP led to increased strength, while the smaller particle size HSP-containing samples decreased in pick strength (**Fig. 6**). Additionally, by choosing the correct HSP type, one could feasibly change binder chemistries to impact other properties while maintaining strength.

HSP Blends	1	2	3	4	5	6
	Parts	Parts	Parts	Parts	Parts	Parts
#1 clay	85.00	85.00	85.00	85.00	85.00	85.00
TiO_2	15.00	15.00				
HSP6			11.75	10.00	9.00	
HSP1			3.25	5.00	6.00	15.00
Vinyl acrylic latex	20.00	17.00	17.00	17.00	17.00	17.00
Total Parts	**120.00**	**117.00**	**117.00**	**117.00**	**117.00**	**117.00**
Coat weight (kraft top, SBS bottom)	3.61	3.69	3.12	3.69	3.64	3.67
	3.05	3.32	3.11	3.01	3.33	3.31
Brightness (on kraft)	71.9	73.9	74.1	74.2	73.9	74.5
Hot melt glueability, %	100	80	100	100	100	76
IGT dry pick strength, VVP	62	54	59	60	60	48

HSP = hollow sphere pigment; TiO_2 = titanium dioxide; SBS = solid bleached sulfate; VVP = viscosity-velocity product.

V. HSP blend formulations and coating properties.

HSP blends

Considering that blends of two different particle size HSPs improved the mechanical strength of thermal paper basecoats, the following studies were conducted to determine whether blending HSPs would provide an improved balance of brightness and strength in paperboard coatings. The same clay formulation was used as a basis for the experiments, and coatings containing HSP1 and HSP6 were prepared. Three blend ratios of both HSPs at 3 parts lower binder showed equivalent IGT dry pick values and glueability as the control (**Table V**). There was very little differentiation in the IGT of the blend ratios, but the brightness increased with HSP1 content, similar to previous data. Since the strength remained unchanged, the blends provide further benefit of brightness beyond using the large HSP alone.

SUMMARY

The following is a summary of findings from Part 2 of this study:

- There is a benefit in the brightness/strength balance when large particle size HSPs are used to replace TiO_2 in paperboard coatings, even though large particle size HSPs have lower light scattering efficiency than small particle size HSPs.
- Adding a large particle size HSP to a TiO_2-containing master batch coating also showed improved IGT values and maintained glueability, to a point. Similar additions of small particle size HSP or TiO_2 resulted in decreased strength. Although this is not how one would typically formulate, it demonstrates the im-

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About this journal

ABOUT THE AUTHORS

We studied this topic because we saw an interesting trend in using hollow sphere pigments (HSPs) to impact the strength of thermal paper coatings and wanted to extend that knowledge to the paperboard space. As first author of this paper, I have worked with HSPs for many years to understand their insulation qualities and impact on thermal print performance.

The most difficult aspect of this research was learning that the existing trends in HSP particle size packing were not consistent with previous work. The complexity of the inorganic pigment systems made it difficult to model, so we leaned into generating the data experimentally.

Through this work, it was gratifying to discover that there is always something new to learn, even in a field where a tremendous amount of research has already been done. Our most interesting finding was the ability for a single HSP to show a dramatic impact on strength across a wide range of coating formulations.

Mills can potentially use this information to optimize their coatings for opacity and strength. With the experimental data we now have in hand, we'd like to go back and see if the systems could be modeled in order to predict further benefits from these materials or others.

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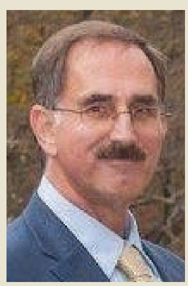

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provement in strength when adding a large particle size HSP to a paperboard coating.

- Further research was conducted to show that the effect is consistent with different binder chemistries. In fact, by incorporating the large particle size HSP, one could feasibly change binder chemistries to impact other properties while maintaining strength.
- The blends of two HSPs also proved interesting, showing further brightness benefits while maintaining strength. **TJ**

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