Using classical theory to design a pigment with improved optical properties

PETER BURRI, CHRISTIAN NAYDOWSKI, DANIEL C. SPIELMANN, AND ERNEST T. SWANSON

ABSTRACT

Ground calcium carbonate is a common coating pigment for paper offering technical and economical advantages. Its high brightness often reduces opacity. This requires adding pigments with high scattering coefficients. Using light-scattering theories, the authors designed a ground calcium carbonate pigment to optimize opacity. Because this pigment had certain disadvantages, they prepared a compromise material using modified grinding technology. That material maintained the current advantages of ground calcium carbonate while shifting particle size distribution and average particle size toward that of an ideal opacifying pigment.

Application:

A new ground calcium carbonate pigment has a low specific surface area and narrow particle size distribution. It offers higher brightness, improved opacity, and better gloss.

FOR THIRTY YEARS, GROUND CALCIUM carbonate (GCC) has been a coating pigment for paper because of its well-know technical and economical advantages. These include the ability to coat at higher solids, increased brightness, reduced binder demand, improved coater runnability, and excellent printability.

The advantage of high brightness coating pigments often leads to reduced opacity. It therefore is necessary sometimes to use other pigments with high scattering coefficients to reach desired opacity. The same phenomenon is also true for hydrous clays that have scattering coefficients similar to that of GCC.

The theories of Kubelka-Munk, Mie, and Weber can explain this phenomenon. Pigments with high brightness, broad particle size distribution, and average particle size near GCC do not provide optimum opacity when coating glossy papers.

We have used light-scattering theories to design a GCC pigment to optimize opacity. In doing this, we found a reduction in many advantages of the present pigments. There was a significant negative influence on runnability, binder demand, and solids content of coatings using the "ideal opacifying GCC." Therefore we made a compromise to retain as much as possible the present advantages of GCC in the new pigment while shifting particle size distribution and average particle size toward that of the ideal opacifying pigment. The manufacture of this pigment was possible by using a modified grinding technology.

End users require improved appearance of the finished, printed product. Higher brightness, opacity, and gloss can accomplish that improvement. The paper manufacturer wants a higher quality product without sacrificing runnability or economics. Meeting the requirements of both the end user and the producer using a new coating pigment requires very careful design.

THEORY

Brightness

Brightness is a very important optical property in coated paper today. Besides the brightness of the base paper, the coating pigments largely determine the brightness of the final product.

The brightness of the pigment depends heavily on the natural origin of the raw material. For instance, the brightness of a GCC pigment depends on whether its origin is chalk, limestone, or marble.

Opacity

For the papermaker, the availability of a pigment that can influence not only the brightness but also the opacity offers new options to optimize paper quality. The parameters that influence the light-scattering power of coating pigments are particle diameter, particle size distribution, and refractive index. **Figure 1** shows the influence of particle size on light scattering. The following equation is the mathematical relationship for the curve in Fig. 1:

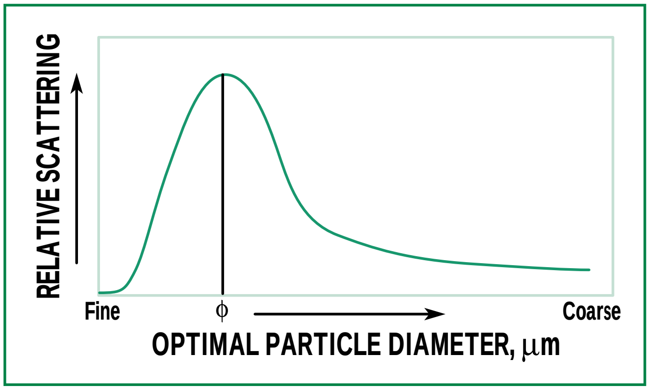
$$\theta = f(\lambda/\Delta n) \qquad (1)$$

where

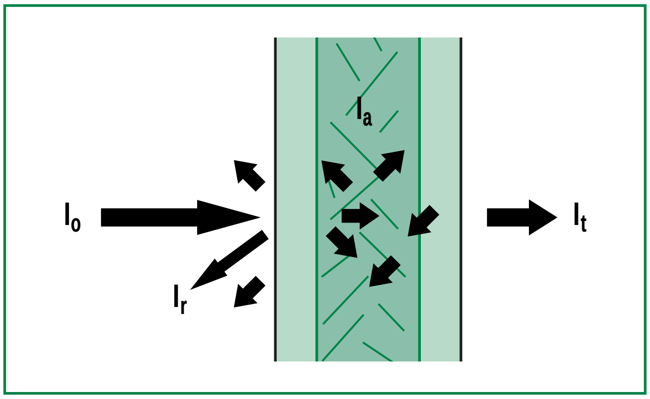
θ = particle diameter
f = system dependent constant
n = refractive index
λ = wave length of incident light.

Lord Rayleigh in 1871 described the light scattering of very small particles or colloidal solutions *(1)*. Tyndall did similar work, and Fresnel studied the reflection of light on the irregular surface of small particles.

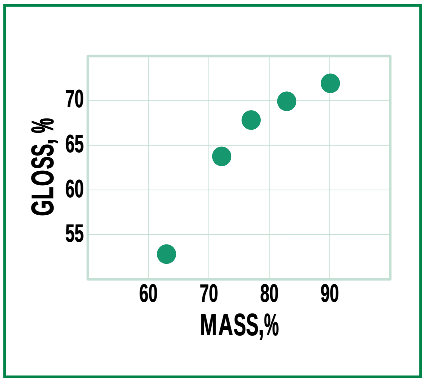
When the dimension of the scattering particles is large compared to the wavelength, the theory of scattering becomes more complicated. We must then consider interference between light waves scattered from different parts of the same particle. Mie described the basis for such light scattering in 1908 for spherical particles *(2)*. His theory gives quantitative information about the relation between



1. Particle size vs. light scattering



2. Behavior of incident light on paper



3. Gloss as a function of particle size

scattering coefficient, diameter, and the refractive index of a white pigment and the wavelength of light.

Weber *(3, 4)* concluded from Mie's theory and Van de Hulst's deviation that the following equation gives the relationship for maximum light scattering between the diameter and refractive index of a particle and the wave length of light:

$$2r = \lambda/f(n_p - n_B) \qquad (2)$$

where

2r = particle diameter
λ = wave length at maximum scattering
n_p = refractive index of pigment
n_B = refractive index of diluent.

Using an approach parallel to the classic theory of light scattering in dilute solutions, Kubelka and Munk *(5–7)* created a basic theory to describe the optical properties of light-scattering and light-absorbing mediums. If light of intensity I_o illuminates the surface of a paper having a thickness Δx, only the three possibilities in **Fig. 2** can occur. There may be reflected or back scattered light, I_r, returning to the side where it was incident. There may be absorption, I_a, disappearing internally with conversion to heat. The final alternative is transmission, I_t, passing through the paper and out the other side. If the paper is sufficiently thick or within a stack of sheets, there will be no light transmission. This is a brief description of the light energy balance that the differential equations developed by Kubelka and Munk summarizes.

Kubelka and Munk assumed that the illumination of the sample and the light propagation within the sample is diffuse. The sample is no longer an isolated particle but a group of interfering particles in an infinite plane with a given thickness. In practical applications, the magnitude of the wavelength of the incident light is important.

Using the Kubelka-Munk theory, it is possible to obtain formulas to describe opacity and brightness *(8)*. Two parameters are necessary: the light-scattering coefficient, S, and the light absorption coefficient, K. The appendix gives the mathematical formulas of the Kubelka-Munk theory for the application to optical properties of paper.

Gloss

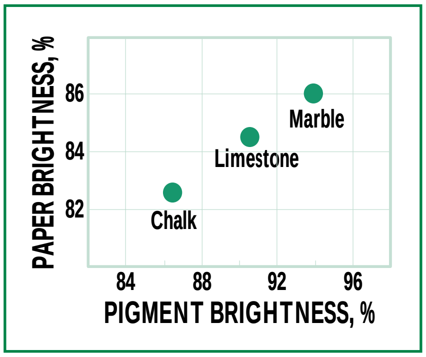
Gloss is the seeming quality of mirror-like, reflected light. In optical terms, gloss is a geometric attribute of the reflection of light by surfaces. The intensity of the reflected light depends on the angle of observation and on two characteristics of the reflecting surface—refractive index and its roughness *(9, 10)*.

For a coated paper, the smoothness of the finished surface largely determines the gloss. Fine, platey clay particles aligned after calendering or ultrafine calcium carbonate are the favorite choices to achieve a glossy surface. **Figure 3** shows the effect of particle size on gloss.

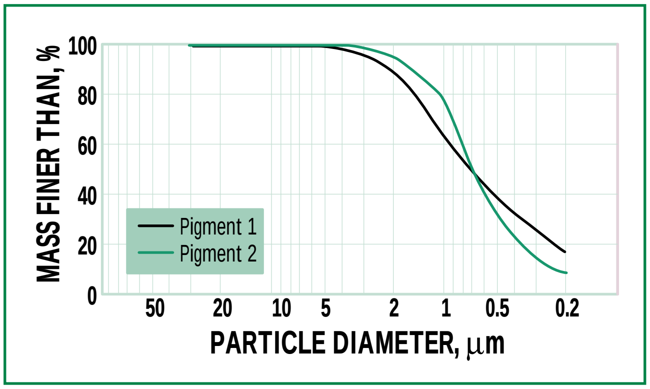
Rheology

The relationship between the rheological behavior and the runnability of a coating color is complex and depends on many factors. The flow characteristics depend on the particle shape, particle size, and particle size distribution of the pigments and solids content and other factors.

After Poisson *(11)* and Stokes *(12–14)* published experimental and theoretical results of their research work on the behavior of liquids, Einstein *(15)* was the first to describe the mobility of particles in solution. Recent years have seen study of flow behavior in highly concentrated suspensions using computer simulation models due to the complexity of the system. Several publications *(16–18)* describe numerical simulation and modeling of coating colors to define important information about physical mechanisms determining the microstructure obtained under shear flow. This information helps explain



4. Paper vs. pigment brightness



5. Particle size distribution for pigment 1 and pigment 2

	Scattering coefficient, m^2/kg	Specific surface area, m^2/g	Wet void volume, %
Pigment 1	81	12.0	16
Pigment 2	139	8.5	27

I. Comparison of physical characteristics influencing opacity

the influence of different parameters on the coating process.

Conclusions from theory

Considering all these theoretical aspects, a new coating pigment with improved optical properties should have the following design:

- For the highest brightness, the raw material—GCC in this work—must be as bright as possible.
- For high opacity, the target particle size distribution should be narrow with a mean diameter of 0.6–0.8 µm. All particles having the same size would be optimal.
- For best gloss, a surface with low roughness is necessary. A fine spherical pigment with a broad particle size distribution will give a smooth surface.
- For fluidity at high solids content, a broad particle size distribution and a spherical shaped pigment would be desirable.

Attempting to build a pigment meeting all four requirements creates a conflict. The particle size and size distribution for opacity contradict the needs for fluidity and runnability. Too narrow particle size distribution could also be detrimental to gloss development.

Earlier publications also mentioned this conflict. Papers from various authors *(19–23)* showed the influence of particle shape and particle size of precipitated calcium carbonate (PCC) on the optical properties of different coated paper grades. Crawshaw *(19)*, Ishley *(21, 22)*, and Engström *(24)* reported rheological performance of a coating color containing PCC or blends with clay and their impact on coating structure and paper properties. In this paper, we will describe the performance of a natural GCC for coating with optimized properties.

DEVELOPMENT

Brightness

GCC pigment production offers a choice of raw material supply. Following are the descriptions for the calcium carbonate deposits used for manufacturing pigments for the paper industry:

- Chalk is a fine, sedimentary material of nanofossils with a brightness of approximately 82–88%.
- Limestone is a compacted form of carbonate based shells from snails and mussels normally found with a brightness of 88–92%.
- Marble is recrystallized chalk or limestone usually having brightness above 95%.

Figure 4 shows the correlation between the pigment brightness of chalk, limestone, and marble and the impact on the brightness of coated paper. Each coating in the figure contained 100% calcium carbonate as the pigment. Application was 10 g/m^2 on a base paper with a brightness of 81.9%. We measured brightness according to a TAPPI Test Method using commercially available equipment.

For our design of an optimized pigment, we chose marble as the raw material. This would yield the pigment with the highest brightness.

Opacity

Using a modified grinding technology, we engineered a pigment with a more narrow particle size distribution. **Figure 5** compares the particle size distribution of a traditional, ultrafine GCC (pigment 1) to an improved material (pigment 2).

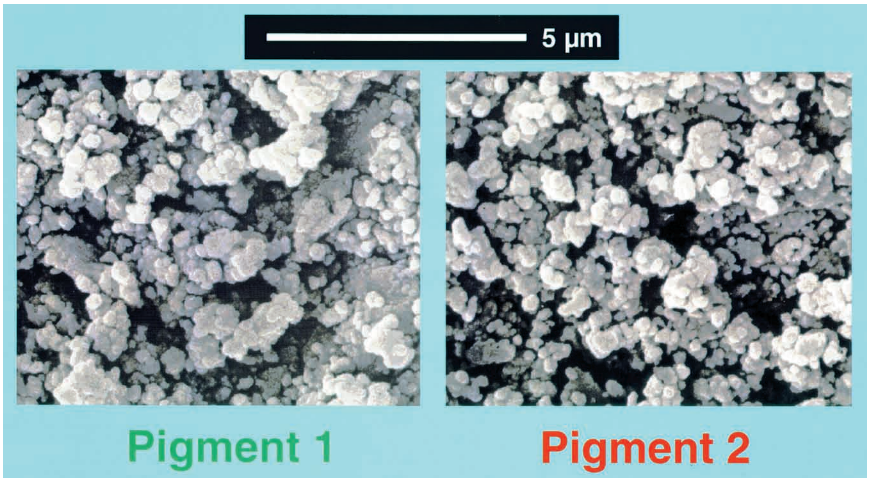
To demonstrate further that pigment 2 should give improved opacity compared to the traditional pigment 1, we measured the scattering coefficient, wet void volume, and specific surface area of both materials. We determined scattering coefficients by applying a defined coating layer on Morest charts. Using the Kubelka-Munk theory, we measured the reflection of light over a white and a black background to calculate the scattering coefficients. The wet void volume is the volume of the liquid in a compact-

100 parts	Solids content, %	Brookfield viscosity, mPa·s @ 100 rpm	Water retention, s for 1 drop
Pigment 1	64	810	38
Pigment 2	64	840	25
70/30 parts			
Pigment 1/clay	66	1940	86
Pigment 2/clay	65	1200	43

II. Comparison of rheological indicators for pigment 1 and pigment 2

Base paper 50 g/m²	Control	Trial
Pigment 1, pts.	60	-
Pigment 2, pts.	-	60
High surface area clay, pts.	40	40
SBR latex/starch, pts.	8/5	8/5
Resin, pts.	0.2	0.2
Dispersant, %	0.15	0.15
Solids content, %	61.3	60.7
Coating weight, g/m²	12	12
Coater speed, m/min	1400	1400

III. Coating formulas for substitution of traditional pigment 1 with pigment 2 for improved paper properties



6. SEM picture for pigment 1 and pigment 2

ed pigment sample after centrifugation. We centrifuged pigments dispersed at 60% solids content for 4 h at 3200 rpm. The difference between the volume of the compacted material and the theoretical volume of the unground mineral is the wet void volume.

Measurement of the specific surface areas of the two pigments followed the method of Brunauer *et al.* *(25, 26)*. This involves absorbing a monomolecular layer of nitrogen on the surface of the pigment. The amount of nitrogen used determines the specific surface area.

Table I shows our results. The scattering coefficient of pigment 2 is approximately 75% higher than the traditional pigment 1. The wet void volume is 55% higher for pigment 2. Pigment 2 has a specific surface area 30% lower than pigment 1.

Gloss

Earlier theory predicted that the optimal GCC pigment for gloss would be spherical with a broad particle size distribution and a small mean particle diameter. Practice has supported this.

Pigment 2 retained the approximately spherical shape and average particle diameter of pigment 1 as the scanning electron microscope (SEM) results in **Fig. 6** show. The particle size distribution curve is more narrow but still contains particles throughout the range of pigment 1. Although engineering of the pigment improved opacity, there should be a minimum impact on gloss.

Rheology

For optimal fluidity, a broad particle size distribution of spherical particles is desirable. As stated above, pigment 2 retains this morphology. The reduced amount of fine particles and narrowed particle size distribution causes a small drop in the maximum solids content for the coating color compared with pigment 1. **Table II** compares solids content, Brookfield viscosity, and water retention for pigment 2 and pigment 1 at 100 parts and in a 70/30 blend with a high gloss clay. The coating colors contained 100 parts of pigment, 11 parts of synthetic binder, and 0.5 parts of cobinder.

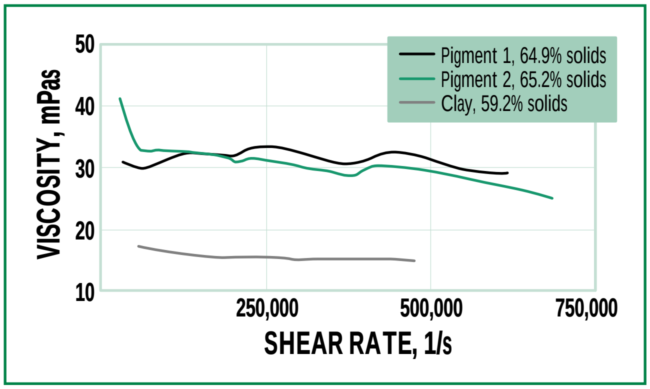
A method of the American Petroleum Institute determined the water retention capability. The time evaluated was the time until the first drop fell from the filter support.

Figure 7 shows rheological properties measured by the Eklund capillary viscometer under high shear rates. At the same solids contents for both pigment 1 and pigment 2, the high shear viscosity for pigment 2 is greater due to the narrower particle size distribution. Pigment 2 has a viscosity similar to a natural delaminated clay but at 6% higher solids content.

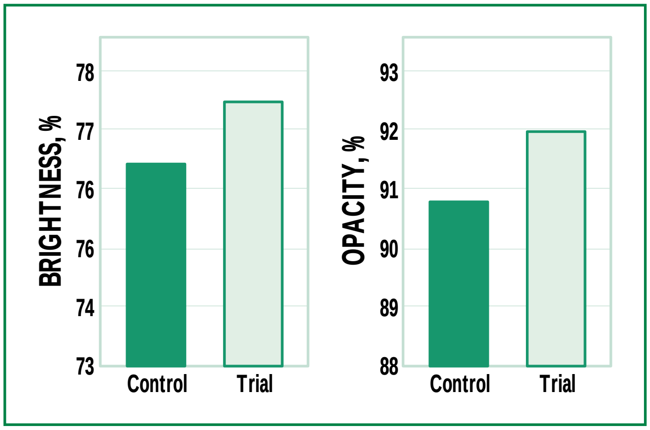
In summary, pigment 2 should give improved opacity and similar brightness compared to pigment 1 and should have a minimal influence on gloss and rheology. To test the design of this pigment, we performed some

KEYWORDS

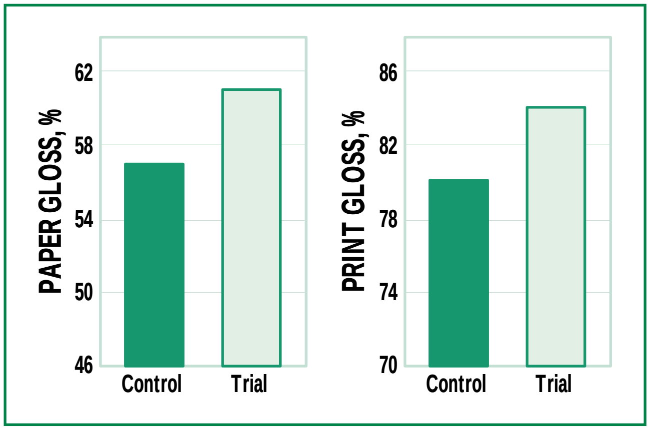
Bibliographies, calcium carbonate, calcium compounds, carbonates, coating color, coloring materials, equations, kubelka munk equation, optical properties, optical scattering, particle size distribution, physical properties, pigment, product development, scattering, specific surface, theories.



7. High shear viscosity for pigment 1, pigment 2, and clay



8. Brightness and opacity for wood containing papers



9. Paper gloss and print gloss for wood containing papers

Base paper 73 g/m²	P1	P2	T1/P1	T2/P2
Pigment 1, 90% <2 µm	-	-	80	-
Pigment 2, 75% <1 µm	-	100	-	80
Pigment 3, 60% <2 µm	100	-	-	-
High surface area clay	-	-	20	20
SBR latex	8	8	12	12
Starch	8	8	-	-
Solids content, %	65.6	61.6	68.2	65.3
Coating weight, g/m²	10	10	11	11
Viscosity, mPa•s	1400	580	1010	630

IV. Coating formulas for improved paper properties for 115 g/m² wood free sheet offset

pilot trials. Results from these trials tested the validity of our approach to pigment engineering.

PRACTICAL EXPERIENCE

Our work included pilot coater trials replacing pigment 1 by pigment 2. We used wood-containing papers and wood-free papers.

Wood-containing papers

Table III describes the coating formulations for the trial. Sixty parts of pigment 2 substituted for the same amount of pigment 1 in a formulation used to coat 75 g/m² wood-containing offset paper. There were no other changes to the formulations. Coating technique was an applicator roll followed by rigid blade metering. Coater speed was 1400 m/min. Final moisture content was 4.5%. Drying was electrical infrared (IR) followed by air foils. The two coated paper rolls underwent supercalendering using identical conditions with a nine-roll reversing nip pilot scale supercalender. Temperature was 80°C, line load was 205 N/m, and speed was 400 m/min.

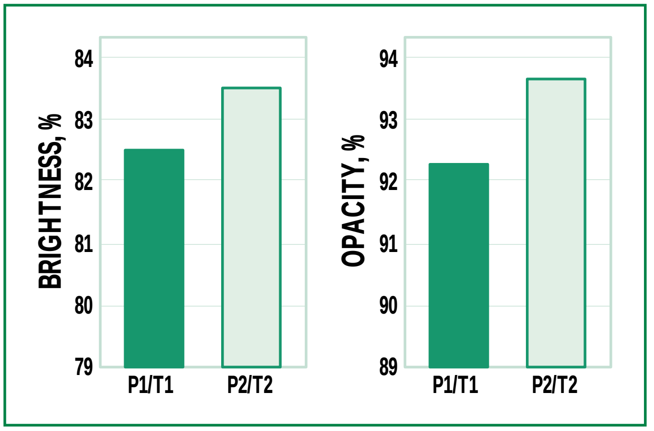
We tested the papers for optical and physical properties and printed them using the Rochester Institute of Technology (RIT) four-color web offset press. **Figures 8 and 9** show the test results. Brightness and opacity of the sheet containing pigment 2 improved by 1%. Gloss was 4–5% higher. While there was a decrease in wet pick strength for the sheet using pigment 2, this did not impact the printability on the RIT press. Print gloss improved slightly for the pigment 2 sheet.

Wood-free papers

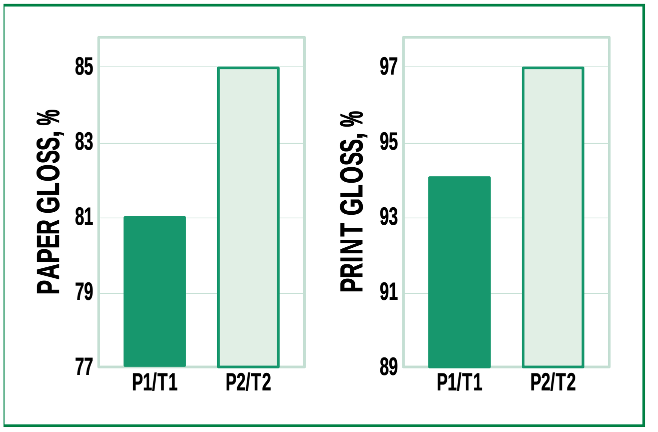
We determined the impact of pigment 2 in wood-free double-coated offset papers for improved optical properties. This involved substituting pigment 2 for the normal pigment 3 (calcium carbonate, 60% < 2 µm) in the precoat and pigment 1 (calcium carbonate, 90% < 2 µm) in a double coated offset sheet. **Table IV** gives an overview of the coating formulations. We hoped to improve brightness, opacity, gloss, and print gloss without using traditional opacifying or glossing pigments.

The trials used a pilot coater in Oftringen, Switzerland. The precoating technique was an applicator roll and rigid blade, and the topcoating technique was an applicator roll and bent blade at a machine speed of 1200 meters/min. Drying was electrical IR followed by air foils. The papers underwent calendering on a nine-nip supercalender under identical conditions. Temperature was 80°C, line load was 150 N/m, and the speed was 400 m/min.

Figures 10 and 11 show the test results. Brightness improved 1% and opacity 1.5%. Paper gloss and print gloss improved approximately 3–4%.



10. Brightness and opacity for wood free papers



11. Paper gloss and print gloss for wood free papers

CONCLUSIONS

In response to the requirements of papermakers and end users for improved brightness and opacity of coated papers, we have used the basic theories of light interaction with pigments to design an improved GCC. Our pigment has a low specific surface area and narrow particle size distribution. These characteristics result in higher brightness, improved opacity, and better gloss. By translating theory to practice, we developed a modified grinding technology. That technology allows the manufacture of the new pigment offering improved optical properties. **TJ**

Burri is vice president coating and printing, Naydowski is senior vice president research and development, and Spielmann is director—research and development paper for Plüss-Staufer AG, Baslerstrasse 42, CH 4665, Oftringen, Switzerland. Swanson is regional technical manager for OMYA inc., 61 Main St., Proctor, VT 95765.

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APPENDIX

The following are the equations for the Kubelka-Munk theory applied to the optical properties of paper:

$$R_\infty = 1 + K/S - [(K/S)^2 + 2(K/S)]^{1/2} \quad (3)$$

$$R_0 = 1/[a + b \coth(bSW)] \quad (4)$$

$$R_{n+1} = \{1 - R_n[a - b \coth(bSW)]\}/[a - R_n + b\coth(bSW)] \quad (5)$$

$$O_p = R_0/R_\infty \quad (6)$$

where

R_∞ = reflectance of a stack of samples for which a further increase in thickness does not change with reflectance

R_{n+1} = reflectance of a sample with a background having a reflectance of R_n

R_0 = zero reflectance of a sample with an ideal black background

S = Scattering coefficient, m^2/kg

K = light absorption coefficient, m^2/kg

W = basis weight of paper, g/m^2

a = constant = 1 + K/S

b = constant = $(a^2 + 1)^{1/2}$.