

Modeling coating structure development using a Monte Carlo deposition method

Part 2: Validation of the model and case study

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ABSTRACT: In Part 1, we introduced a 3-D particle-deposition model based on a Monte Carlo deposition method to simulate coating structure development during coating consolidation. In Part 2, the model predictions are compared with experimental results as well as results from available literature. More specifically, the effects of particle size and its distribution on porosity, pore size, and surface micro-roughness are investigated. The comparison shows that the model predicts well the important features of the effects of pigment properties on coating porous structures. Therefore, this model can be a powerful tool for papermakers in designing coating formulations to maximize product performance and reduce the cost of materials. As an example, a case study demonstrates how to manipulate pigment size distribution to improve both print and paper gloss in offset printing.

Application: A computer model that simulates the development of coating structure is a time-saving and cost-effective way to identify the best pigments and pigment combinations.

In Part 1 [1], we introduced a 3-D particle-deposition model based on a Monte Carlo deposition method to simulate coating structure development during coating consolidation. The model relies on the minimization of the total energy of the particle system, which is defined as a sum of three terms: a pair interaction that can account for collisional and colloidal interactions, a gravitational potential energy, and a *drag potential energy* that takes into account the drainage rate of the color.

To summarize Part 1, the particles are deposited under the actions of both the gravity and a "drag force" field from an initial configuration representing the wet film of the pigment suspension applied onto the paper. Once the total energy is minimized, the resulting particle packing can then be characterized in terms of such properties as porosity, pore size, and surface micro-roughness. This model has the potential to take into account the Brownian motion, dewatering rate, irregular particle shapes, and interparticle interactions.

In Part 2, we will compare the model predictions with experimental results and data from available literature. In addition, we will demonstrate the usefulness of this approach in a case study that will show how to manipulate pigment size distribution to improve both print and paper gloss in offset printing.

MODEL VALIDATION

Based on the methodology described in Part 1, a computer program has been written in Fortran 90, and the simulations have been performed on a PC-based parallel computer. Each numerical data point given here is made up of an average of at least 20 simulations in order that we may report statistically reliable results. The size of the domain used for the simulations was at least 5 times the diameter of the biggest particles in the case of mono-sized and binary mixtures and at least 3 times the size of the biggest particle in the case of polydispersed mixtures. We found that these domain sizes were sufficient to avoid any influence of the domain size on the porosity.

Viscosity, Pa·s	0.02
Drainage rate, m/s	1.10^{-6}
Max. translation distance, m	1.10^{-8}
Temperature, K	293.15
Borosilicate density, kg/m ³	2230
TiO ₂ density, kg/m ³	4000
Starch density, kg/m ³	1500

1. Parameters used for the simulations.

Depending on the case studied, the simulations lasted from a few seconds to a few hours on a single processor. **Table I** presents the different parameters used for the simulations. We chose relatively small values for the drainage rate parameter and the maximum translation distance

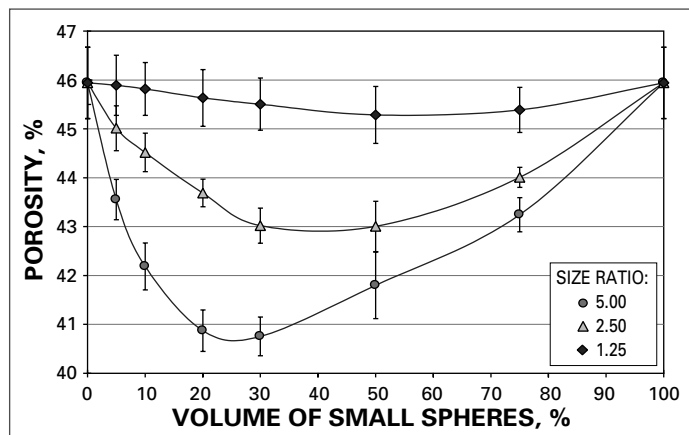
in order to emulate slow deposition occurring on impervious substrates such as Mylar.

Packing of mono-sized spheres

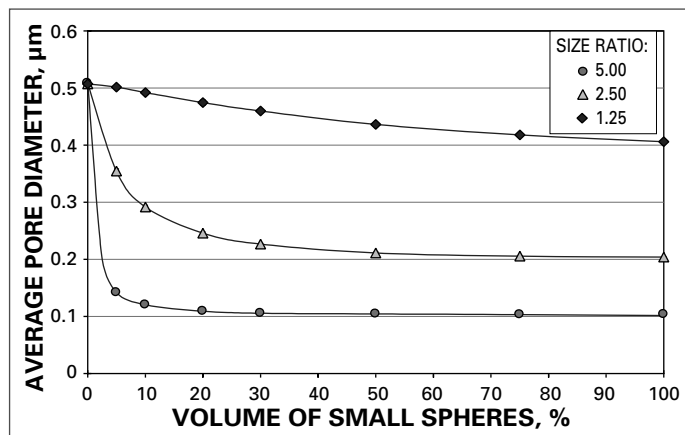
To compare our program first with previous experimental and numerical works, we performed simulations of a simple packing of 0.5 μm mono-sized spheres. **Table II** summarizes the results.

The porosity value obtained with our deposition model is in good agreement with the porosity value reported by Buchalter and Bradley [2] for a 3-D packing of spheres using a similar Monte Carlo technique. Dullien [3] defined this range of porosity as very loose, typical of porosity obtained by sedimentation of spheres. Our deposition model created a looser packing than the one obtained numerically by Eksi and Bousfield [4-6]. We attribute this difference to interparticle interaction that induces bridging effects. The pore size distribution we obtained (not shown here) was slightly wider than the one obtained by Eksi and Bousfield, creating a slightly higher number of small and big pores (percolation and bridging effects). The difference in pore size distribution explains why the average pore diameters are identical even though the porosities are different.

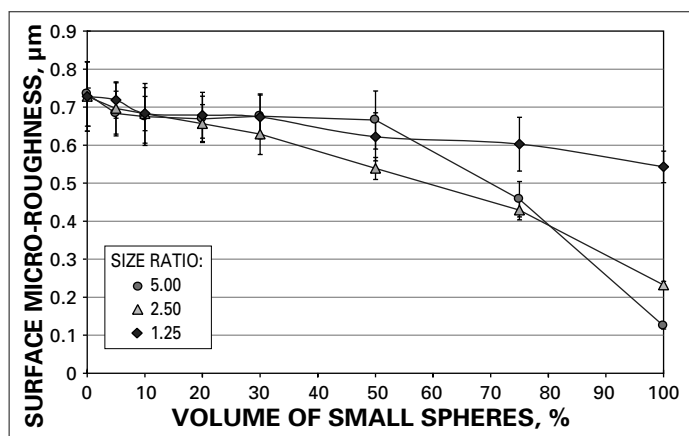
Porosities obtained from coatings of 0.5 μm plastic pigments [7,8] were much lower than those obtained numerically. We believe that this difference can be explained either by the actual polydis-



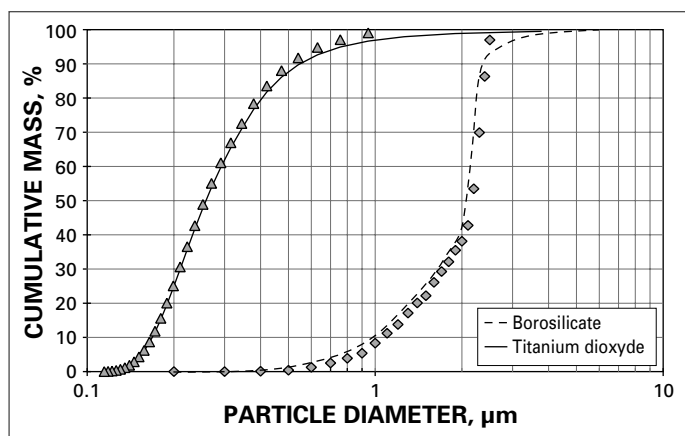
1. Variation of the packing porosity with respect to the volume of small spheres and the particle size ratio, as computed by our deposition model (coat weight = 10 g/m²).



2. Variation of the average pore diameter with respect to the volume of small spheres and the particle size ratio, as computed by our deposition model (coat weight = 10 g/m²).



3. Variation of the surface micro-roughness with respect to the volume of small spheres and the particle size ratio, as computed by our deposition model (coat weight = 10 g/m²).



4. Borosilicate and titanium dioxide size distributions. (The symbols represent the discretizations used for the simulations.)

persity of the pigments they used [8], by the softness of the plastic pigments, or by formation of "ordered" pigment clusters due to attractive colloidal forces. (In all simulations reported at this stage, we assumed that interactions were between hard core particles).

As we will show, our model accurately predicts experimental porosities when the experiments are performed with undeformable pigments under conditions that guarantee the absence of attractive colloidal forces (i.e., pH ≥ 8). Finally, the surface micro-roughness values obtained by our simulations compare well with those obtained in Eksi and Bousfield's model when the values are computed with the same algorithm.

Packings of binary mixtures of spheres

Packings of binary mixtures of spheres were performed at various mixing ratios and different diameter ratios. Specifically,

Simulations	POROSITY, %	MEAN PORE DIAMETER, μm	MICRO ROUGHNESS, μm
Our model	45.9 ± 0.7 44.3 ± 0.7*	0.254 ± 0.002*	0.365 ± 0.044 0.165 ± 0.025*
Buchalter, Bradley [2]	46.5	—	—
Eksi, Bousfield [3-5]	40.0	0.254	0.135
Experiments			
Alince, Lepoutre [6]	33.1	—	—
Leskinen [7]	36.5	—	—

*Computed using Eksi and Bousfield's characterization algorithm.

II. Comparison of computed microstructure parameters of a 0.5 μm sphere packing with previous works.

particles of 1 μm in diameter were mixed with small particles of 0.8, 0.4, and 0.2 μm. **Figure 1** presents the results of packing porosity for the various combinations. The occurrence of a minimum porosity was predicted. The volume of small spheres at which this minimum porosity occurs depends on the particle size ratio. This trend is in complete agree-

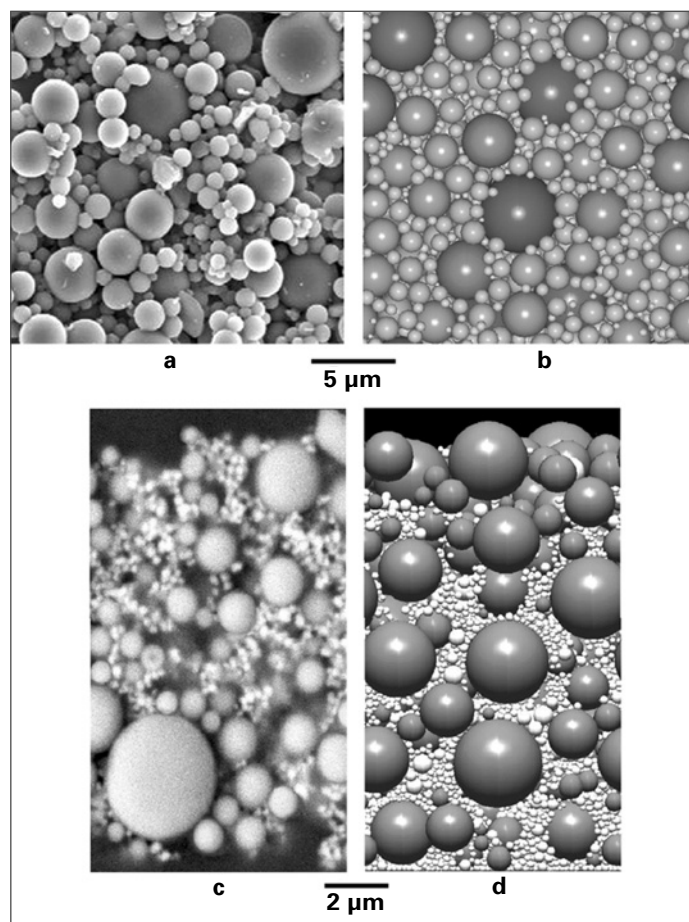
ment with experimental and numerical data found in the literature [9-11]. The significant change in porosity resulting from mixing spheres of two different sizes emphasizes the need for a tool to predict the coating structure of mixtures of polydispersed pigments.

Figures 2 and 3 present respectively the change of average pore diameter and

Porosity	COLOR 1	COLOR 2
Deposition model, %	37.6 ± 0.4	36.0 ± 0.7
Deposition model, corrected for binder, %	31.2 ± 0.4	28.3 ± 0.8
Experiments, %	32.0 ± 1.7	28.7 ± 0.4
Avg. pore diameter		
Deposition model, μm^*	0.643 ± 0.007	0.346 ± 0.001
Experiments, μm^{**}	1.013 ± 0.013	0.382 ± 0.006

*Equivalent spherical diameter. **Equivalent cylindrical diameter.

III. Comparison between experiments and simulations.



5. Micrographs of coatings comparing experiments (a, c) and simulations (b, d). Views a and b are top views of the Color 1 coating. Views c and d are cross-sections of the Color 2 coating.

surface micro-roughness with the particle mixing ratio. The simulation results indicate that adding a very small amount of small-sized particles into large-sized particles drastically reduces the pore size. However, the change in micro-roughness is rather gradual. These findings are in good agreement with numerical [4-6] and experimental [7, 8] data published in the literature.

In the case of micro-roughness, increasing the mixing ratio with a particle size ratio of 5 gave actually a somewhat different trend than with particle size ratios of 1.25 and 2.5. Before decreasing gradually, the micro-roughness stayed constant until a certain mixing ratio. This behavior is explained by the fact that after a certain size ratio, the small particles are smaller than the

pores formed by the big particles. Hence, the small particles percolate into the structure, preventing the further reduction of the surface micro-roughness until the pores are completely filled with the small particles. High polydispersity of the pigment blend should eliminate this phenomenon.

Packings of polydispersed pigment blends

To validate our deposition model with well-controlled experiments, we applied two model coating colors on Mylar using a bench-scale blade coater. The coat weight was $13.0 \pm 1.0 \text{ g/m}^2$. The two coating formulations were prepared at 60.5% solids content and a pH of 8.0 and had a 7 pph starch content as binder. The first color had a 100% borosilicate pigment content, whereas the second color had pigment content of 80% borosilicate and 20% titanium dioxide by volume. Borosilicate pigments were especially chosen for their spherical shape, whereas the shape of titanium dioxide pigments is roughly spherical.

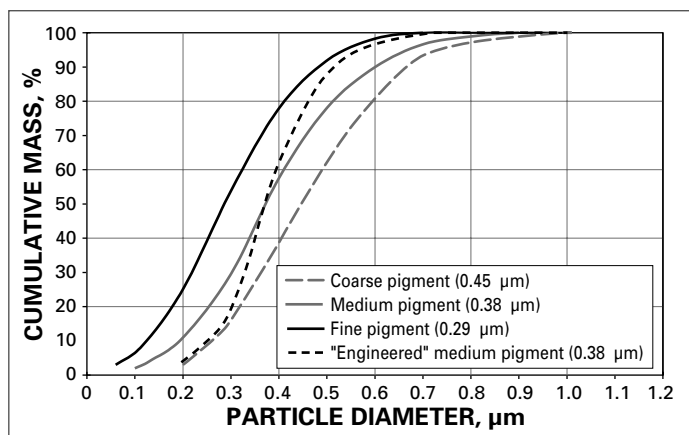
Figure 4 presents the particle size distributions of the two pigments. The average pigment diameters (based on frequency) for borosilicate and titanium dioxide are 0.93 and 0.20 μm , respectively. We used totals of 261 particles for Color 1 and 8692 particles for Color 2.

Mercury intrusion porosimetry has been performed on the two coated samples. Experimental porosities and average pore diameters are compared in Table III with the numerical data extracted from our deposition simulations. As expected, the numerical porosity values were higher than the experimental ones. However, if we consider that the binder is trapped into the pores of the coating and correct the numerical porosity values accordingly, the resulting values agree very well with the experimental porosities. In terms of pore size, the deposition model predicts a significant reduction with the addition of 20% titanium dioxide (Color 1 to Color 2), similar to the experimental results. However, a direct comparison between the experimental and numerical values is difficult because of the difference in the definition of "pore" between the two methods and because of the presence of binder in the pores of the real coating.

Figure 5 presents micrograph for comparing the real coatings and the simulations. The top and cross-section views look quite similar. However, there are some subtle differences. Clustering of particles can be seen in the micrographs for the experiments but not in those for the simulations (even though the pH was adjusted at 8). The clusters seem to create a somewhat rougher and looser structure than the structure used in the simulations. (Note that this cluster formation can be implemented in the deposition model.) Nevertheless, the current model captures the main packing effects on coating structure development and accurately predicts general trends.

CASE STUDY

For many coating grades (such as lightweight coated), both high sheet gloss and high print gloss are desired in offset printing. However, in a recent publication, Donigian *et al.* [12] showed experimentally that decreasing the average diameter of a precipitated calcium carbonate (PCC) pigment increases the paper gloss as expected, but it decreases the print gloss. This outcome was attributed to the fact that smaller pores resulting from finer pigments at a constant porosity cause a faster ink set-



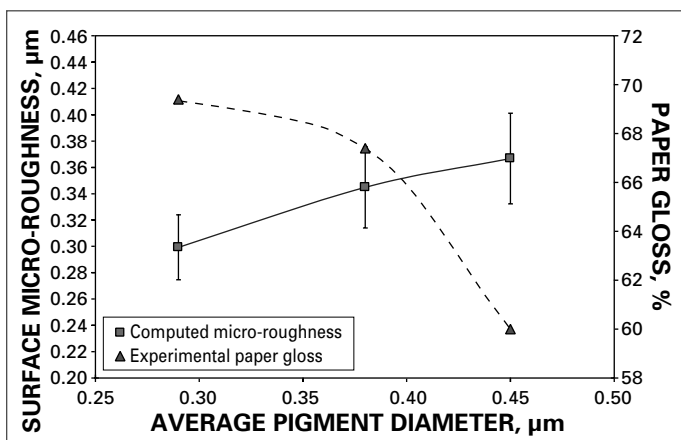
6. Particle size distributions of the pigments studied. (Values in parentheses represent average particle diameters.)

ting and thus a lower print gloss. This phenomenon is explained by Desjumeaux *et al.* [13] and Xiang and Bousfield [14] in terms of a higher capillary pressure available from small pores to overcome the ink pigment filtercake resistance. Therefore, to achieve both high paper gloss and high print gloss, one needs to increase micro-smoothness without reducing the pore size.

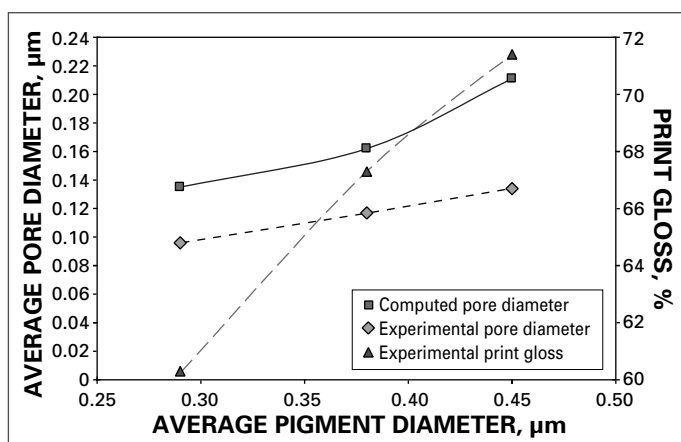
To deal with this issue, we first performed deposition simulations with three of the pigments used by Donigian *et al.* [12] and named them coarse, medium, and fine pigments with respect to their sizes (Fig. 6). Since the tails of two particle size distributions were incomplete in the original publication, they have been extrapolated. For this reason and also because of the discrepancy in pore size definitions and the presence of binder, the experimental and numerical results can only be compared qualitatively (i.e., in terms of trends). Since the shapes of the PCC pigments are close to spherical, we believe that approximating the pigments using spheres is reasonable for the purpose of this study.

As expected, the deposition model predicted an increase in surface micro-roughness with increasing pigment size (Fig. 7), which corresponds to a decrease in paper gloss, as observed experimentally. The increase of pore size with increasing particle size is also in qualitatively good agreement with the experimental data obtained from mercury intrusion (Fig. 8). Furthermore, as noticed by Donigian *et al.* [12], the print gloss seems to increase when pore size increases (Fig. 8). Therefore, shifting the particle size distribution towards higher or lower particle size is not the solution for achieving both high paper gloss and print gloss.

An alternative approach is to modify the particle size distribution of the pigment. In a test simulation, we narrowed the particle size distribution of the medium pigment and kept the average particle size constant. We named this new pigment "engineered" pigment. As shown in Fig. 9, narrowing the particle size distribution simultaneously increases the pore size and decreases the surface micro-roughness. Based on this finding, we expect that the engineered pigment gives higher print and paper gloss in offset printing. This result also indicates that the use of so-called "engineered" pigments marketed recently by pigment suppliers is indeed an effective way to enhance both sheet gloss and print gloss [15].



7. Comparison between computed surface micro-roughness and experimental paper gloss (experimental values from Donigian *et al.* [12]).



8. Comparison between computed and experimental pore sizes, and experimental print gloss (experimental values from Donigian *et al.* [12]. (Pore sizes are calculated from the published mercury intrusion curves.)

CONCLUSIONS

The model predicted well the important features of the effects of particle size and distribution on porosity, pore size, and surface micro-roughness. The optimization of the particle size distribution to simultaneously improve print gloss and paper gloss demonstrates the usefulness of such a modeling. Simulation is a time-saving and cost-effective way to identify the best particle size distribution to yield the desired properties of the coating.

This approach can also be used to optimize pigment blends in order to maximize product performance and eventually reduce the cost of the materials. Moreover, it can give us some insight as to why one formulation performs better than another. **TJ**

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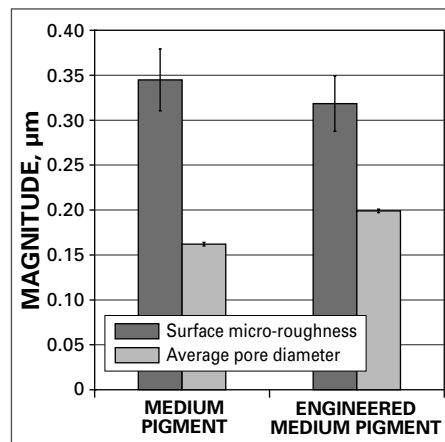
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9. Comparison in terms of micro-roughness and pore size between the original and engineered pigments.

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INSIGHTS FROM THE AUTHORS

Our model needed to take into account irregular-shaped particles, the drainage of the fluid phase, and interparticle interactions. It also had to be able to simulate the deposition of a realistic number of particles within a reasonable time frame.

We realized that a deterministic approach based on Newton's second law would fail to achieve these goals because of the prohibitive number of computations required to determine the particle trajectories. A Monte Carlo deposition method appeared to be a better trade-off, since we could expect the deposition of concentrated suspensions to be more of a stochastic process than a deterministic one.

In retrospect, the deposition of concentrated suspensions does appear to be suitably described by the stochastic deposition model because of the high level of collisions of Brownian particles. A deterministic approach based on Newton's second law would not be likely to improve the accuracy much, and the computations involved would be more demanding on computer resources and take more processing time.

A case study shows how this simulation model can be used to help design coating formulations to improve

product performance and reduce the costs. The objective was to improve both print and paper gloss in off-set printing. A simulation of a modified, or "engineered," pigment showed that both can be achieved by manipulating pigment size distribution.

This model is a preliminary version, and some features need to be implemented more fully. We plan to present the improved particle deposition model with refinements and new features at the next TAPPI Advanced Coating Fundamentals Symposium in Chicago.

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