Modeling coating structure development using a Monte Carlo deposition method Part 1: Modeling methodology

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ABSTRACT: Designing or formulating new coatings with improved performance or lower cost is a complex task. The current industrial practice for coating formulation takes a trial-and-error approach, with pilot-scale trials or lab-scale coating experiments. This approach neither guarantees finding the best formulation nor gives any insight as to why one formulation performs better than another. In this paper (Part 1), we introduce 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. It has the potential to take into account the Brownian motion, dewatering rate, irregular particle shapes, and interparticle interactions. The model predictions are compared with experimental and available literature data in Part 2 of this report, which will appear in next month's *TAPPI JOURNAL*.

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.

For decades, the main approach to designing new coatings with improved performance or lower cost has been to conduct pilot-scale trials or laboratory-scale coating experiments. Usually, several pigments of different size distributions and shapes are tried with various binders during a coating trial. Moreover, pigments are frequently blended to achieve the properties that a sole pigment cannot provide on its own. There are, then, a tremendous number of variables and combination of variables to be taken into account.

Even with an adequate experimental design, it requires enormous time and cost to find the optimum coating formulation. For this reason, the design of a new coating formulation is often a trial-and-error procedure, which neither guarantees finding the best formulation nor gives any insight as to why one formulation performs better than another. Therefore, there is a need for a systematic, cost-effective approach that can predict the end-use performance of coated papers and help optimize coating formulations.

Predicting the performance of coated papers relies on two aspects of analysis. First, we have to identify the key coating structures that control the specific end-use performance. Fortunately, there is already in the literature a good knowledge base of the coating structures required for such properties as paper gloss, print gloss, opacity, permeability, and adhesion [1–6].

Second, we have to model the development of the coating structure. Pioneering works [7–10] have raised the interest in modeling the development of coating structure based on particle-packing. However, these models suffer from important limitations such as the inability to account for irregularly shaped particles, the effects of drainage rate, and interparticle interactions during the deposition process.

Consequently, our objective was to develop a model that can predict coating structures in terms of pigment size distribution, shape, and consolidation conditions. Although the model we present here is in its early stages, it can predict consistent results with existing models and experimental findings and can capture some important features of coating structure development.

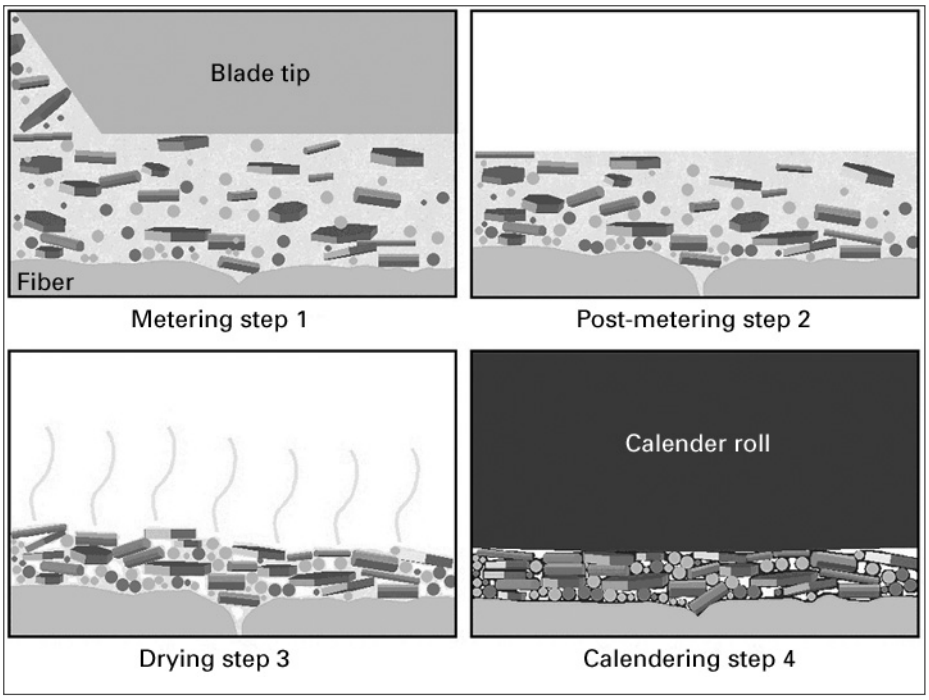
REVIEW OF COATING STRUCTURE DEVELOPMENT

Coating colors are applied as aqueous suspensions at high speeds. As shown in **Fig. 1**, the consolidation of the coating structures typically occurs in several steps. First, the coating is applied and metered onto the paper. Second, the water in the coating is removed by drainage into the basestock and by evaporation, resulting in the formation of a three-dimensional particle structure. Third, upon drying, latex particles deform, causing the structure to shrink. Fourth, in most cases, a calendering stage is used, which further compresses the coating structures.

Coating consolidation is essentially a particle-deposition process, but it is affected to a certain extent by dewatering and particle redistribution as a result of drying and calendering. Any modeling or computer simulation of coating structure development must capture these features as well.

The development of coating structures depends on many variables, such as pigment and binder properties, basestock properties, and coating and drying processes. Over the years, a number of studies have been carried out [11–17]. The following key factors have been identified as important to coating structure development:

- Pigment properties (average particle size and distribution, and particle shapes)
- Interparticle interactions (e.g. collisional and colloidal interactions)
- Coat weight
- Dewatering by paper
- Drying conditions.



1. Coating structure development.

Among these factors, the pigment properties are the most important and can be changed the most conveniently.

REVIEW OF COATING STRUCTURE MODELING

Over the past thirty years, many analytical and computer models have been developed in various fields (e.g., powder processing, mining, painting) to study suspensions, granular flows, and particle-packing [18–35]. However, there have been only a very limited number of modeling studies with regard to paper coating [7–10, 36–38]. Most of these modeling studies have dealt with predicting the maximum viscosity of a color suspension or the average porosity of a dry coating, without giving any information on local structure.

Recently, Eksi and Bousfield [7–9] developed the first 3-D particle-packing model to simulate the coating consolidation process. This model consists basically of dropping spheres sequentially from random positions above a growing pile of spheres and allowing the dropped spheres to roll over the pile until they reach a stable three-point contact. Although a number of simplifications and assumptions were made, the packing model gave good predictions on porosity, pore size, and coating shrinkage, particularly in terms of trends. The model represents a promising systematic approach to simulating and characterizing the development of a coating structure. However, further improvements are needed in the areas of (a) interparticle interactions and the effect of dewatering rate and (b) the consideration of particle shapes.

Interparticle interactions and the effect of dewatering rate.

A fundamental problem in simulating coating consolidation is describing the process by which particles deposit. Procedures for sequential deposition have been used in previous models and are reasonable for dilute suspensions. However, the approach completely neglects interparticle interactions (such as hard core collisions), which become significant at high dewatering rates during the deposition of concentrated suspensions. Indeed, Lepoutre [15] showed that high dewatering rates increase particle size segregation in the packing. An improved packing model should take into account interparticle interactions during the deposition process and should include a representation of the fluid phase that entails such properties as the viscosity of the fluid phase and the dewatering rate. These features could help us understand the effects of additives such as thickeners and other polymers.

Consideration of particle shapes.

Because of its simple geometry, the sphere has been used as the main particle shape in previous modeling work. A few studies have actually focused on the three-dimensional packing of aspherical particles such as spheroids, cylinders, and parallelepipeds, and in all cases the size distributions of particles were mono-dispersed [26, 34]. However, coating pigments have many different particle shapes, including platelets, needlelike particles, and rhomboid particles, and their particle size distributions are essentially polydispersed. The particle shape has a significant effect on the packing structures [39]. Therefore, it is important to incorporate the effect of particle shape into the packing simulation.

To contend with these problems, we have designed a new deposition model to simulate the development of coating structure during coating consolidation.

MODELING METHODOLOGY

Rosato *et al*. [22] introduced a Monte Carlo model to understand a size segregation problem known in the granular matter field as the "Brazil Nuts" segregation. The pouring phase of this model consists of positioning circular particles at random in a 2-D box and letting them drop simultaneously by means of a "downward-oriented" random walk procedure. The original 2-D model was based on disks dropping under the action of a gravitational field. We have adapted the model to take into account the presence of the fluid phase and the resulting drag force exerted on the particles, and we have expanded the original 2-D model to a 3-D model.

Deposition model

The particles are first located at random in a box (that we will call the "domain") having periodic boundary conditions in directions perpendicular to the z axis, or the drainage and gravity direction (**Fig. 2**). The size and the number of particles located in the domain depend on the particle size distribution of the pigments, the color solids content, and the coat weight. The height of the domain is equal to the wet film thickness of the coating. The random distribution of the particles is postulated on the assumption that the initial suspension is well dispersed.

Any other distribution can be easily implemented at this stage to reflect a specific poorly dispersed state.

Let the configuration of a system of N particles be denoted by the generalized coordinates of the particle centers:

$$\tilde{c} = \{\boldsymbol{c}_1, \boldsymbol{c}_2 \ldots, \boldsymbol{c}_N\} \tag{1}$$

where $\boldsymbol{c}_j = (x_j, y_j, z_j)$ represents the location of the jth particle. Let $E(\tilde{c})$ denote the total energy of the system. In our case, the particles drop under the actions of both the gravity and the drainage of the fluid phase in which the particles are suspended. For drainage rates encountered in coating, a dimensional analysis can show that the gravitational term is not negligible and becomes important with respect to the drag term for particles bigger than 2–5 microns. The drag force generated by the draining fluid phase brings the particles downward. The effect of the fluid phase can be seen as the effect of, what we could call, a "drag force field". Hence, the total energy of the system is the sum of three terms:

$$E(\tilde{c}) = U(\tilde{c}) + E_g(\tilde{c}) + E_d(\tilde{c}) \tag{2}$$

where $U(\tilde{c})$ is the pair interaction, $E_g(\tilde{c})$ the gravitational potential energy, and $E_g(\tilde{c})$ the *drag potential energy*.

Let us now define more precisely these three potential energies. The interaction between two adjacent hard spheres, say i and j, is characterized by a pair interaction $U_{ij}(\boldsymbol{c}_i, \boldsymbol{c}_j)$ given by:

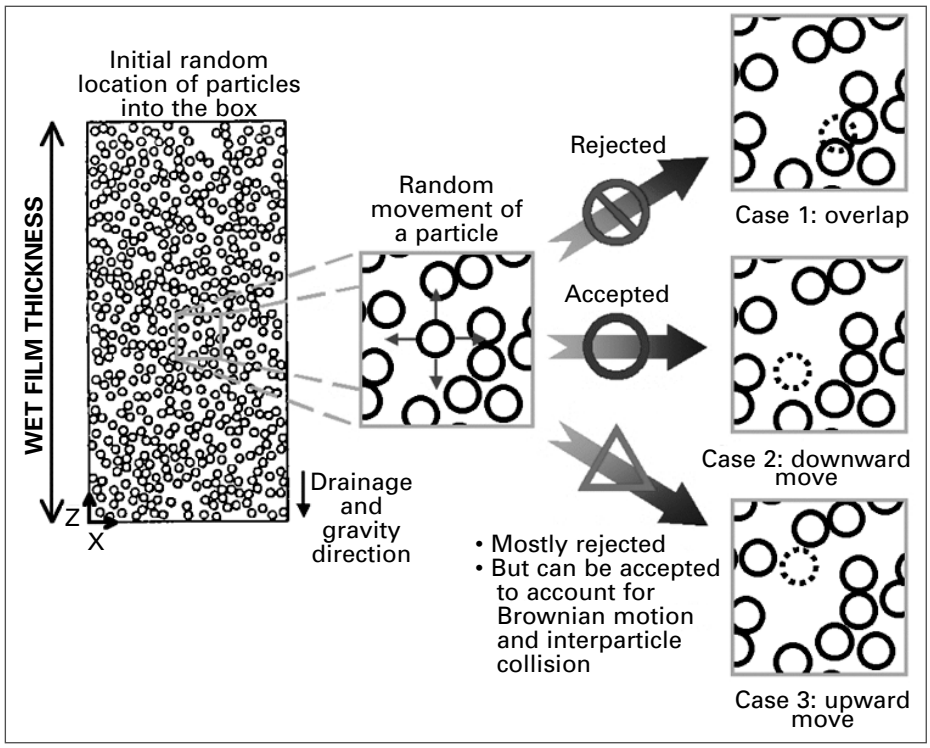
$$U_{ij}(\boldsymbol{c}_i, \boldsymbol{c}_j) = \begin{cases} 0 & if \quad |\boldsymbol{c}_i - \boldsymbol{c}_j| \geq r_i + r_j \\ \infty & if \quad |\boldsymbol{c}_i - \boldsymbol{c}_j| < r_i + r_j \end{cases} \tag{3}$$

where r_i and r_j are the particle radii and $U_{ij}(\boldsymbol{c}_i, \boldsymbol{c}_j) = 0$ for $i = j$. This pair interaction prevents the adjacent particles from overlapping. Hence, the total pair interaction of the system can be expressed as:

$$U(\tilde{c}) = \tfrac{1}{2} \sum_i \sum_j U_{ij}(\boldsymbol{c}_i, \boldsymbol{c}_j) \tag{4}$$

Next, the gravitational potential energy of a hard sphere system is given by:

$$E_g(\tilde{c}) = \sum_{j=1}^{N} v_j \, \Delta\rho_j \, g \, z_j = \sum_{j=1}^{N} \frac{4\pi r_j^3}{3} \Delta\rho_j \, g \, z_j \tag{5}$$



2. General behavior of the Monte Carlo procedure (2-D representation).

where v_j is the volume of the jth particle, $\Delta\rho_j$ is the density difference between the jth particle and the fluid phase, and g is the gravitational acceleration.

Finally, the drag potential energy of a hard sphere system is defined as:

$$E_d(\tilde{c}) = \sum_{j=1}^{N} C_j \, \mu V \, z_j = \sum_{j=1}^{N} 6\pi r_j \, \mu V \, z_j \tag{6}$$

where μ is the fluid phase viscosity, V is a drainage speed parameter, and C_j is a drag coefficient equal to $6\pi r_j$ for spheres. The idea behind the drag potential energy term is to establish a "drag force field" similar to the gravitational field that forces the particles to move in the drainage direction, thanks to the use of an energy minimization procedure.

The Monte Carlo method works by analyzing the probability P that the various configurations $\tilde{c}$ will occur. The Boltzmann distribution gives us this probability:

$$P[E(\tilde{c})] = \frac{1}{Q} \exp\left[-\frac{E(\tilde{c})}{kT}\right] \tag{7}$$

where Q is the partition function of the system, T is its absolute temperature (taken, for example as the ambient temperature), and k is the Boltzmann constant.

Starting from an initial distribution of particles in the domain, particles are moved one at a time within a small neighborhood characterized by a maximum translation distance taken usually as $0 < \delta < {}^2/_{\sqrt{3}} \times \min(r_j)$. Hence, a trial position for particle j is given by:

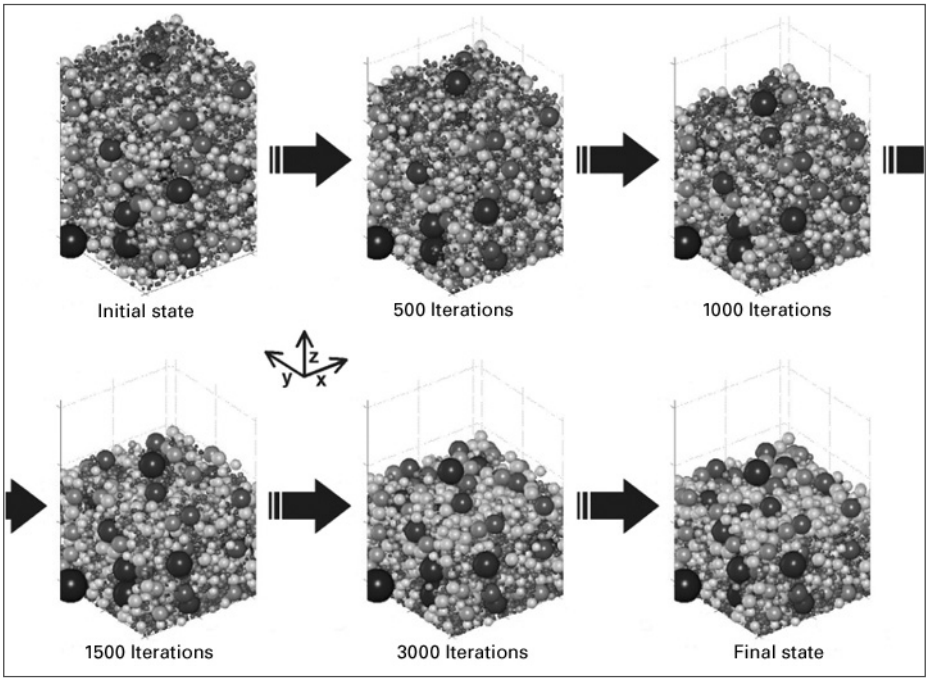
$$\left.\begin{aligned} x_j' &= x_j + \xi_x \, \delta \\ y_j' &= y_j + \xi_y \, \delta \\ z_j' &= z_j + \xi_z \, \delta \end{aligned}\right\} \quad with \ -1 \leq \xi_x, \xi_y, \xi_z \leq 1 \tag{8}$$

where ξ_x, ξ_y, ξ_z are uniformly distributed random numbers.

Thus, from the initial configuration $\tilde{c}$, a trial configuration $\tilde{c}'$ is generated, which is unconditionally accepted as the new configuration if $\Delta E = E(\tilde{c}') - E(\tilde{c}) \leq \varphi$, where $\varphi = 0$ in the original model from Rosato et al. [22]. However, as proposed by Dippel and Luding [40], we took $\varphi = 0.05$ to allow for slight upward motions that can take place due to interparticle collisions. In the case where $\Delta E = E(\tilde{c}') - E(\tilde{c}) > \varphi$ then $\tilde{c}'$ is accepted if $\xi \leq P[\Delta E]$, where ξ is a uniformly distributed random number and $0 \leq \xi \leq 1$, and $P[\Delta E]$ is a probability given by:

$$P[\Delta E] = \frac{P[E(\tilde{c}')]}{P[E(\tilde{c})]} = \exp\left(\frac{-\Delta E}{kT}\right) \tag{9}$$

If $\xi > P[\Delta E]$, then the trial configuration is rejected and the original configuration is retained.



3. A sequence of states obtained using the Monte Carlo procedure.

The procedure for updating the packing configuration is carried out for each particle move, and its net behavior is summarized by Fig. 2. Moves that lead to an overlap with neighbor particles are automatically rejected because $\Delta E = \infty$. Downward moves are automatically accepted because $\Delta E < 0$. Most upward moves are rejected. However, for submicron particles, $\Delta E/kT$ becomes very small, and according to Eq. 9, the probability of upward motion increases significantly. This increase allows us to account for Brownian motion, which for small particles is strongly related to μV, or the fluid phase viscosity and the drainage rate. Thus the addition of the drag term to the original formulation is necessary in order to relax the system into a packed structure. Without this term, submicron and micron-sized particles would always vibrate and would never deposit.

Once an attempt to move all N particles has been made, one iteration is completed. The simulation is stopped when no particle has moved for one or more consecutive iterations. **Figure 3** presents a typical sequence of states obtained during the iteration process. Note, as discussed by Rosato *et al*. [22], that the evolution of the simulation in Monte Carlo "time" (i.e., an iteration) gives us a "time-dependence" that can be, at this point only, compared qualitatively with the one observed in real coating systems. Moreover, Buchalter and Bradley [25] claimed that increasing the maximum translation distance δ is similar in effect to increasing the deposition rate.

We found that high values of δ lead to size segregation (that is, small particles tend to migrate more into the structure) and create a somewhat more porous, more disordered structure. Lepoutre [15] observed a similar behavior with substrates of high absorbency. This seems to confirm a relationship between δ and the drainage rate, although more work is needed to quantitatively correlate them. Actually, the vector (V, δ) should in fact serve as the drainage rate parameter since V and δ are correlated. (In an improved version of the current model, δ is the only drainage rate parameter, and V is calculated at each iteration from the average particle move generated by the given δ).

While the procedure described is intended for spheres, extension to irregular-shaped particles is feasible using special efficient algorithms to detect overlap between super-ellipsoids or polyhedra, such as the ones encountered in computer games and virtual reality fields. These algorithms can be implemented to replace the conditions of Eq. 3. The drag coefficient for spheroids and needle-like particles can also be found in the literature [41]. Buchalter and Bradley [25–26] have performed simulations of 2-D and 3-D mono-dispersed ellipsoids using a slightly different Monte Carlo technique.

Note that repulsive or attractive forces between the particles (e.g. colloidal forces) are not taken into account at this stage in the current model but can be simulated by choosing appropriate pair interactions (Eq. 3). One can also argue that a constant velocity profile is assumed in the model. However, we believe that a detailed velocity profile would not give more accurate results because of the approximations usually taken (such as for the smoothness of the particles) and that the deposition of highly concentrated suspensions is more a stochastic phenomenon than a purely deterministic one. However, to simulate the deposition under a blade, a shear velocity component could be added. Finally, note that the model does not take into account at this stage the possible film-forming of latex particles, nor does it take into account the consolidation and the compression exerted onto the coating by surface tension phenomena and calendering.

Pore space characterization

Once a packing structure is obtained using the Monte Carlo technique, it needs to be characterized in terms of such traits as porosity, surface micro-roughness, average pore size, and pore size distribution. We compute porosities on x–y cross sections of the packing and average the values to obtain the 3-D packing porosity. The x–y cross-section porosity is obtained by computing the intersection area of the particles with the x–y plane and subtracting it from the x–y cross-section area of the domain.

Surface micro-roughness is computed using an algorithm similar to the one used by Eksi and Bousfield [7]. The domain is divided into identical vertical subdomains in which the highest vertical position of the packing is determined. The surface micro-roughness is taken as the standard deviation of those highest points. As an x–y subdomain size, Eksi and Bousfield used the radius of the biggest particle. However, we found that using the radius of the largest particle leads to misleading results when polydispersed pigments have to be compared. We therefore prefer to use the radius of the smallest particle.

For the calculation of the average pore size and pore size distribution, we use the same approach as Eksi and Bousfield used [7]. The computational domain is discretized using a tetrahedral mesh in which each tetrahedron vertex corresponds to a center of a particle. A pore is then defined as the free space within a tetrahedron, which is, as defined, bounded by four particles. Thus, the pore volume is equal to the difference between the tetrahedron volume and the volume of the four particle sections located inside the tetrahedron. From this volume, an equivalent spherical pore diameter can be calculated for each pore. Very recently, Toivakka and Nyfors [42] have introduced a new algorithm that gives more accurate pore size distributions, although the average pore size seemed very close to the one generated by Eksi and Bousfield's algorithm. This new algorithm is fully compatible with our model and could be used in the future to characterize the pore space of our packings.

CONCLUSIONS

A 3-D particle-deposition model based on the Monte Carlo deposition method has been developed to simulate the development of coating structure as the coating consolidates. 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.

Unlike previous approaches to modeling particle deposition as a sequence of events, this model has the potential to take into account simultaneously the dewatering rate, Brownian motion, irregular particle shapes, and interparticle interactions. The validity of this approach will be examined in the companion paper (Part 2), where the model predictions will be compared with experimental data and data from other published studies. **TJ**

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INSIGHTS FROM THE AUTHORS

Our objective was to develop an advanced computational model that can predict coating structures in terms of pigment size distribution, shape, and consolidation conditions. Other works have pioneered the mathematical modeling and computer simulation of the development of coating structures based on particle packing. However, these models suffer from limitations such as the inability to account for irregularly shaped particles, for the effects of drainage rate, and for interparticle interactions as the particles deposit.

Although the model we are presenting is in its early stages, it is consistent with results from existing models in the case of spherical particles and is is validated by experimental findings. Moreover, the model can capture some important features of coating structure development.

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

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