# Watching Paint Dry: A 2D Model of Latex Film Formation

William T. Vetterling*
Zink Imaging, Inc.
*Corresponding author:  16 Crosby Drive, Bedford, MA, william.vetterling@zink.com

**Abstract:** Coating machine operations are often performed with water-based fluids to avoid the environmental problems and expense associated with the disposal of organics solvents. A typical water-based coating fluid contains a suspension or solution of a polymeric binder along with the materials that it will affix to the coating substrate.   When the water in this fluid is evaporated in a dryer, the coated materials are left in the film-forming binder.

This paper presents a 2D model for the drying of the binder.  The results are compared to a prior 1D model by Kiil,[1] and to experimental data from Croll.[2,3]   The 2D model shows the manner in which air flow, which is necessary for the removal of the water vapor, produces a surface profile on the air/water boundary that influences the progress of drying. The model also allows us to evaluate the 2D water vapor distribution, the evaporative temperature depression and the net rate of water removal.

**Keywords:** latex, drying, deformed-mesh, coating

## 1. Introduction

In water-based coating operations, a typical coating fluid usually contains a water-borne suspension or solution of a polymeric binder along with the materials that are to be attached to the coating base.  The water is evaporated in a dryer, leaving the coated materials embedded in the binder.

A suspension of a water-insoluble polymer is known as *latex*, a name commonly associated with water-based paint. It is problematical that latex film drying may limit the speed at which the coatings may be applied.  One issue is that if latex is dried too quickly, it may form a "skin" that inhibits the removal of water from underlying fluids.

The initial latex fluid is composed of nano-sized polymer particles in water suspension. They are held apart by electrostatic or steric forces for stability.  As the fluid is dried, the particles become packed together, and if the drying is above the so-called "minimum film forming temperature", or MFFT, the repulsive forces are overcome to produce a single continuous film.  If the temperature is too high, however, coalescence of the particles may outpace the water removal, leaving behind a film that is permanently soft and tacky[4]

A great deal of work has been carried out to understand the drying process for latex, focusing on the packing of the polymer particles, the transport of water through the porous structure, and the coalescence of the polymer into a final film.[5]  Vanderhoff et al.[6] originally characterized the process as having three principle stages:

**Stage 1:** The wet coating, containing stabilized polymer nano-particles, begins to dry at a rate similar to that of pure water.

**Stage 2:** When sufficient water is removed, the latex particles come into mutual contact and the latex becomes a water-laden porous solid.  At that point, the rate of water removal decreases as the water/air boundary recedes into the solid.

**Stage 3:** The polymer particles coalesce to build a continuous film, and remaining water leaves via any remaining pores, or by diffusion through the polymer.

Several refinements on this fundamental scenario have been proposed.  An example is the relatively recent work of Kiil,[1] who formulated a simple 1D model for the drying process, and demonstrated that it accurately explained two carefully measured data-sets measuring the room-temperature drying of a latex film.[2,3,7] The simplifications in the model arise primarily from assuming that 1) Stage 1 ends when the polymer packing has achieved a polymer fill-factor of 74%, corresponding to the packing efficiency of close-packed spheres, and 2) that the water evaporation in Stage 2 proceeds from the surface downward, separating the porous polymer into a dry porous solid region on top,

and a wet porous region on the bottom. The first assumption removes one of the few variable parameters in the model, and the second assumption (previously proposed by Croll[8]) allows the division of a model into discrete regions that represent, from bottom to top: substrate, wet porous latex, dry porous latex, and air.

Kill formulated his proposal into a 1D numerical model. However, the 1D nature of the model does not capture the position-dependence of the drying that occurs in an air-flow, and such a flow is necessary to carry away the moisture that emanates from the film. We have constructed a COMSOL model to represent Kiil's proposal in 2 dimensions, and used it to take a qualitative look at the progress of drying as it occurs in an airstream.

## 2. Model Description

Fig. 1 shows the starting configuration of the model. A PET substrate carries a latex coating with loosely distributed particles of acrylic polymer in suspension. Above the coating is a region of flowing air for drying.
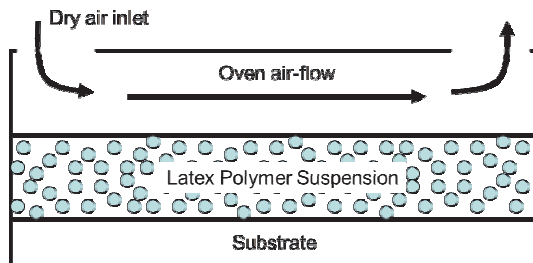


Figure 1. Materials used in this model include a PET substrate, a suspension of acrylic latex polymer, and a region of heated, flowing air.

As time proceeds, the water evaporates and the three layers of Fig. 1 develop into the four regions illustrated in Fig. 2. In this figure, the polymer has been packed into a compact porous structure, and the water/air interface has moved from its original location y3 to a location within this structure. This has divided the packed latex
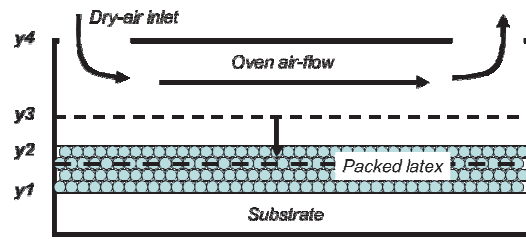


Figure 2. This figure shows the model system with an internal moving boundary (the dashed line) that tracks the air/water interface. In stage 1, the interface is at the surface of the latex coating (upper dashed line). In stage 2, the latex has compacted to 74% fill factor, and the interface has entered the packed structure (lower dashed line). The quantities y1 to y4 represent, respectively, the top of the substrate, the top of the packed latex, the top of the initial wet coating, and the height of the model region.

into a dried portion on top, and a wet portion on the bottom. The layers are then:
- substrate (layer 1)
- wet latex (layer 2)
- dried latex (layer 3)
- air (layer 4)

Although there are four significant layers in the system, we have found it cumbersome to model the geometry in this fashion due to the changing nature of the latex layers 2 and 3. At the beginning of the simulation, there is no dry latex, so layer 3 is a layer that comes into being at some point in the middle of the simulation. Similarly, layer 2 shrinks in thickness as the latex dries, and ultimately disappears. It is clear that a moving mesh is needed to track these changes, but such meshes require special treatment to deal with layers that begin or end with zero thickness.

Instead, we have taken the approach of representing the entire system as a single porous medium, with properties (both material properties and porosity) that vary with position and time. The portion of space occupied by the substrate, for example, is considered to have a porosity of zero, and the portion occupied by air is assigned a porosity of one. The latex coating has variable porosity, and is infused with a fluid that may be either water or air, depending upon location. This approach introduces a slight burden on the user to remember where the

materials are, since there are no boundaries in the model to represent them, but it simplifies the numerical aspects of the problem.

In this single medium we need to apply boundary conditions at the moving air/liquid interface, so the system is divided by a single internal boundary that represents this interface (represented by the dashed lines in Fig. 2). Our model geometry is therefore divided into two regions, loosely described as being the "wet" part and the "dry" part. The "wet" part consists of the substrate and the wet portion of the latex (initially all of the latex). The "dry" part is initially just the oven air, but in stage 2 it comprises both the oven air and the dried portion of the latex.

## 3. Implementation

The model is constructed using COMSOL Multiphysics, and makes use of four modules: 1) Deformed Geometry, 2) Heat Transfer in Porous Media, 3) Free and Porous Media Flow, and 4) Species Transport in Porous Media.

There are several couplings between the modules. The Deformed Geometry module provides the mesh, with a moving boundary that tracks the air-water interface. The boundary implements conditions corresponding to the evaporation of water, causing the boundary to move, and providing a source of water vapor for the Species Transport module. It also accounts for the heat of fusion of the evaporation, which acts as an energy-sink in the Heat Transfer computation.

The Free and Porous Media Flow calculation computes the motion of the oven air, and the result is used by the Species Transport module to evaluate the convective removal of water vapor. The temperatures computed by the Heat Transfer module are used to compute the water vapor pressure at the moving boundary and the temperature-dependent diffusion constant of the water vapor in the air and the dry-latex region, both of which affect the rate of water removal in the Species Transport calculation.

**Fill Factor**

The dry region is initially composed solely of oven air, but when sufficient water evaporates, the fill-factor of acrylic polymer in the latex reaches its maximum value of 74%, and the packed latex begins drying. At this point the air/water interface enters the latex. A single formula for the fill-factor F of polymer that applies to both stage 1 and stage 2 in the dry region is

$$F = 0.74 * (y \leq y2).$$

The reason that this formula is comprehensive is that during stage 1, there is no part of the dry region having $y <= y2$, and during stage 2, the latex in the dry region, where $y <= y2$, is already compacted with fill factor of 0.74

The wet region is a bit more complicated. For $y \leq y1$ the material is a PET substrate with a fill-factor of 1. For $y > y1$, the material is wet latex having a fill-factor that increases as the film dries. Initially, the fill-factor is less than 0.74 and the thickness is greater than the value $d\_latex = y2-y1$ that it has when the latex is packed. When the packed layer reaches a thickness of d_latex its fill-factor has risen to 0.74, where it remains on further drying. We express this fill-factor as

$$F = 0.74*min(1,d\_latex/(y\_boundary-y1)),$$

where y_boundary is the x-dependent y-coordinate of the air/liquid interface. This expression has a numerical problem in that y_boundary goes to y1 at the end of drying, potentially leading to a division by zero. Therefore, we have actually used the expression:

$$F=0.74*min(1,d\_latex/max(y\_boundary-y1, d\_latex/2)),$$

which has the same values but does not overflow. In order to evaluate this expression throughout the wet region, we need to have access to the y-coordinate of the air/liquid boundary for each value of x. To provide this, we have used an extrusion coupling.

**Material Properties**

Since the model boundaries have not been chosen to replicate material boundaries, we need to define explicitly the material properties as a function of spatial coordinates. In the dry region, this is not an issue, since the solid matrix is acrylic polymer and the liquid component is air throughout; only the fill-factor changes. In the wet region, we need to distinguish the material properties of the substrate, for $y < y1$, from the material properties of the acrylic polymer for $y >= y1$. This is necessary only for the Heat Transfer module, since the other modules are activated only in the dry region. The material properties for the wet region are entered as user-defined expressions of the form:

**Thermal Conductivity**:

Solid Matrix:
$$k = k_{polymer}*(y \geq y1)+ k_{substrate}*(y < y1)$$

Liquid:
$$k = k_{water}*(y \geq y1) +k_{substrate}(y < y1)$$

Similar expressions apply to the density, heat capacity and gamma.

The remaining issue is the control of the deformed mesh. The top and bottom surfaces of this mesh are held fixed in both x and y. The two side boundaries are fixed in x, but free in y to allow vertical movement of the mesh points to conform to the vertical motion of the air/water boundary. The internal boundary moves in response to evaporation of the water. In particular, we use the vertical component of the total flux of water vapor to evaluate the amount of water leaving the boundary, and then move the boundary mesh points by the appropriate amount. The mesh velocity is

$$v_{boundary} = \text{-tfluxy} * MW_{water} /\rho_{water}/(1\text{-}F)$$

where $MW_{water}$ is the molecular weight of water, tfluxy is the y-component of total flux, $\rho$ is density and F is the fill-factor evaluated at the boundary.

The flux is the result of a transport calculation in which we assume that the vapor-pressure of water vapor at the moving interface is just the saturation water vapor pressure at the local temperature. The diffusion of this water vapor combines with that of the water vapor of the incoming oven air to produce the final concentration profile, and it is the net vertical flux of this quantity that leads to water removal from the boundary. In order to compute the boundary motion accurately, it is necessary to use the weak form for the flux computation. When the boundary vapor ultimately rises to the temperature and vapor pressure of the oven air, flux disappears and the boundary stops moving.

The implementation just described is not a recasting of the 1D model of Kiil, but rather a 2D model based on the same basic principles. Because Kiil was comparing his model to laboratory data, it was necessary for him to make several simplifications to relate his parameters to the conditions of the experiment. These included:

- The use of average convective heat and mass transfer coefficients over the length of the sample.
- The use of an estimated heat transfer coefficient for natural convection.
- The use of an approximated effective diffusion coefficient of water vapor in a dry porous layer.
- The use of single average temperature values to represent the substrate and the film temperatures.

These quantities were evaluated by reference to correlations reported in previous literature. In the 2D COMSOL model, the simplifications are for the most part unnecessary, as the full 2D behavior is produced from the fundamental differential equations.

A notable exception is the value of the "tortuosity" for gas diffusion in the packed polymer. In the COMSOL model, we used the built-in Millington and Quirk[9] model, though its applicability to coalescing polymers is uncertain. This model was designed as a model of gas diffusivity in soil, and even in that context is not without alternatives.[10] In addition, both the Kiil model and the 2D model are subject to the details of polymer coalescence that may be occurring as the drying proceeds.

## 4. Results

### Airflow

The air flow used for this report enters and leaves through ports in the top boundary, as shown in Fig. 3. This is the type of airflow that may exist in a coating machine dryer, in which conditioned air is sprayed on the coating through jets or slots from an air plenum.
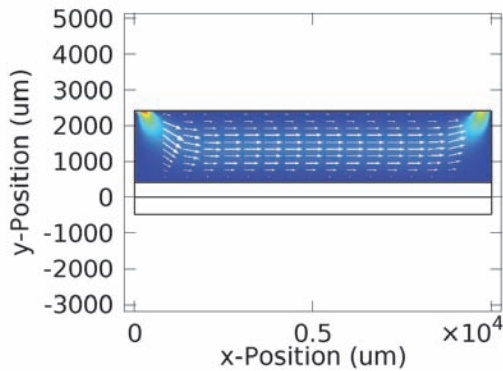


Figure 3. Airflow for a system in which the film is dried through slots that spray conditioned air on the sample.

The inlet air is relatively dry and picks up moisture as it proceeds from left to right. Consequently, the drying proceeds more quickly on the left, and a typical solution has a surface profile for the air/water boundary that develops in the early drying and then marches to the right with further airflow. Figure 4 illustrates such a profile, and how it changes in shape as the simulation proceeds.

A consequence of the profile is that the water vapor leaving the film is typically a mix of molecules that have come both from the wet unpacked latex and from the internal regions of the packed and partially dried latex. Prior 1D models cannot represent this profile and must treat the system as though the air/water boundary is level and receding uniformly into the latex pack.
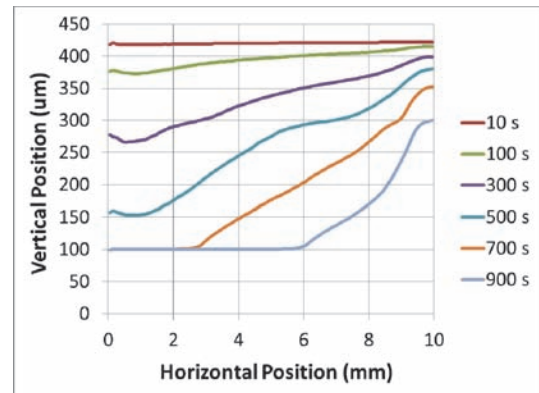


Figure 4. Surface profiles for the air/water interface. The latex dries more quickly on the left, finally reaching the substrate at y=100 um. The curves have slight inflections at y=305 um, which is the top of the packed latex.

### Water Vapor Distribution

The 2D model also provides access to detailed information about other model variables. For example, Fig. 5 illustrates the 2D distribution of water vapor in the oven air flowing to the right. As this air becomes saturated with water vapor near the polymer layer, the flowing air becomes less effective at removing water from the downstream coating. Nevertheless, the continual diffusion of water vapor away from the packed polymer does allow further removal of water at a reduced rate proportional to the concentration gradient.
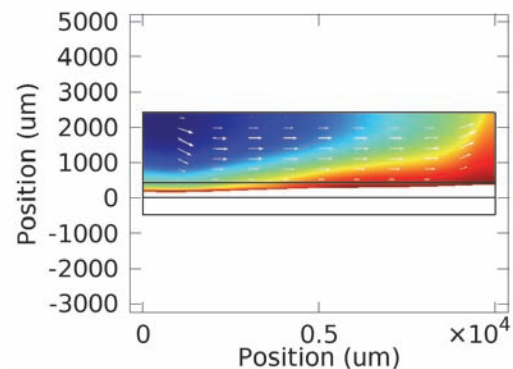


Figure 5. A 2D profile of water vapor concentration. This profile is for t=480 s, about half-way through the drying process.

## Interface Temperature Depression

As water evaporates from the air/water interface, the interface is cooled., and the cooling affects the rate of water removal. In the illustrated example, this temperature depression is small because the air velocity is quite low (approximately 0.14 m/s). Fig. 6 shows the temperature depression as a function of y-coordinate at x=5 mm (the center of the model). Results are shown for several times during the drying. As time proceeds, the position of lowest temperature (the air/water interface) moves closer to the substrate, until finally the coating becomes dried and the cooling decreases to zero.
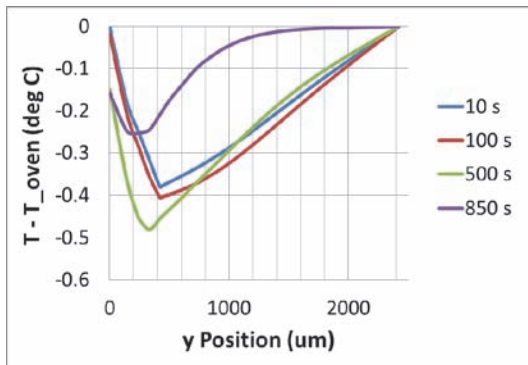
Figure 6. Temperature depression as a function of height along the centerline of the model.

## Wet Fraction

As a measure of progress during the drying, we created a boundary probe named WetFraction that monitors the average value of (y-y1)/d_latex on the air_water interface, where d_latex is the thickness of the packed latex when it has reached a fill-factor of 74%. This quantity begins with a value greater than 1 because the coating has an initial fill factor that is less than 74%. It becomes 1 when the polymer is packed, and then falls toward zero as the film dries further. Note that WetFraction is a measure of water level and not water volume, as it does not compensate for fill factor. Were it not for the increasing diffusion length through dried polymer and the changing temperature of the air/water interface, the time-dependence of this quantity would be linear. Figure 7 shows the actual behavior,

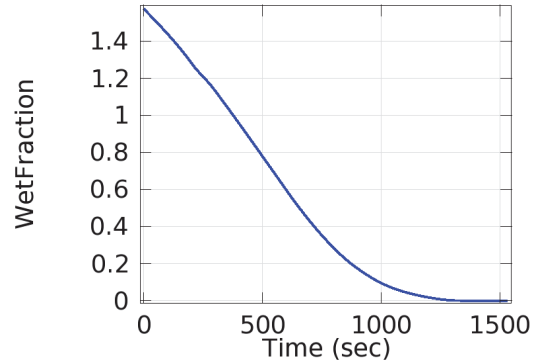which rolls off significantly before the water is entirely removed.

Fig. 7. WetFraction, as defined in the text. A wet fraction of 1.57 in this example, corresponds to the initial coated film. The value 1 indicates the polymer is fully packed with a fill factor of 74%, and the value 0 indicates a fully dried film.

## Total Interface Flux

To evaluate the rate of water loss of the film, we implemented a second boundary probe that integrates the total flux of water from the air/water interface. The graph of this variable in Fig 8 shows some rich detail that is not available to a 1D model. In broad detail, it shows an interval of high water loss for about 200 second, during which the polymer packs. This is followed by a transient and an interval of 300 seconds during which a portion of the interface recedes into the packed latex and ultimately reaches the substrate. Finally, there is a period of about 700 seconds during which the interface increasingly submerges and the film finally dries out.

## 5. Comparison with Data

The Kiil 1D model has been successfully compared to the experimental data of Croll,[2,3] and of Eckersley and Rudin.[7] The data was collected for samples that are much larger in dimension than would be easily modeled in 2D. There are also several ways in which the 2D model differs in assumptions and parameters from the 1D model. Therefore it is unrealistic to
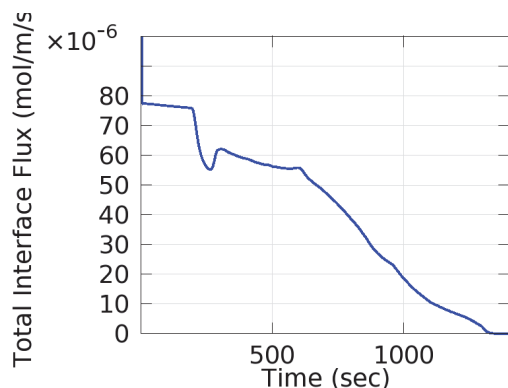
Figure 8. Total rate of water removal. An initial high rate of water loss subsides at t=200 s, when the interface enters the packed latex, and does so again at about t=600 s as portions of the latex become completely dry.

expect precise agreement with the previous work. Nevertheless, it is important to check whether the two models are qualitatively similar.

For this purpose, we note that for a long sample, the airflow has a layer close to the latex surface that is nearly saturated with water vapor. As the air passes down the sample, this layer widens as the water vapor diffuses away from the surface and allows further water evaporation. The width of the saturated layer should develop as sqrt(Dt), where D is the diffusion constant. Based on this picture, we estimate the total water vapor removal per unit time to be proportional to sqrt(vL), where v is the air velocity and L is the sample length. The total drying time should be proportional to sqrt(L/v).

Using a model coating of the same starting thickness and fill factor as one of Croll's samples (i.e. thickness 323 um, fill factor 0.5), we found a total drying time of 1350 s. However, Croll's sample had a sample length of 316 mm and an air velocity of 1.8 m/s. Our model had a sample length of 10 mm and a peak air velocity of 0.14 m/s. Comparing the values of sqrt(L/v) suggests that we should multiply our drying time by ~1.6 to compare with Croll's drying time. We would therefore expect a value of 2160 s. The experimental result was approximately 3000 s.

Kiil noted a similar discrepancy and ascribed it to a probable coalescence of the latex during

stage 2 of drying. For the 1D model, he estimated that the packed polymer fill factor had changed from 74% to 83% while drying, giving a time-average fill factor of 79%. Applying a similar correction to the 2D model would give a drying time of 2674 s. This is an error of about 11%, which reasonable for such a qualitative comparison.

Similarly, a comparison of drying rates, as reflected by the interface temperature depression, can be performed by multiplying our calculated 0.4 deg C depression by the ratio of sqrt(vL) between experiment and model. This leads to an average depression of about 3 deg C, in substantial agreement with Croll's observation of a 2.5 deg C depression.

## 6. Conclusion

We have created a 2D model of latex drying based on the simplified model of Kiil. The model exhibits the effects of air flow in causing differential drying rates across the sample. It also provides detailed temperature profiles, water/air interface profiles, water vapor distributions and drying rates. Qualitative comparison with Kill's 1D model and Croll's measurements indicate consistency at the level of about 11%.

Future work will be aimed as refining the air flow to more correctly represent the conditions that exist in our coating facilities. The model will be combined with a model of latex coalescence to help determine the best oven conditions for efficient drying.

## 7. References

1. Soren Kiil, "Drying of latex films and coatings: Reconsidering the fundamental mechanisms", *Prog. Org. Coat.*, **57**, pp. 236-250, (2006).
2. S. G. Croll, "Drying of Latex Paint", *J. Coat. Tech.*, **58 (734)**, pp. 41-49, (1986).
3. S. G. Croll, "Heat and mass transfer in latex paints during drying", *J. Coat. Tech.* **59 (751)**, pp. 81-92, (1987).
4. J. Baghdachi, "Polymer Systems and Film formation Mechanisms in High Solids, Powder,

and UV Cure Systems", available at:
www.swst.org/meetings/AM04/Baghdachi.pdf

5. P. A. Steward, "Literature Review of Polymer Latex Film formation and Particle Coalescence", www.initium.demon.co.uk/fftext.htm, (1995).

6. J. W. Vanderhoff et al., J. Polym. Sci., Polym. Symp. **41**, 155-174 (1973).

7. S. T. Eckersley and A. Rudin, "Drying behavior of acrylic latexes", *Prog. Org. Coat.* **23**, p. 387, (1994).

8. S. G. Croll, J. Coatings Tech. **58** (734), 41-49 (1986).

9. R. J. Millington and J. M. Quirk, "Permeability of porous solids", Trans. Faraday Soc. **57**, pp. 1200-1207 (1961).

10. P. Moldrup et al., "Three-Porosity Model for Predicting the Gas Diffusion Coefficient in Undisturbed Soil", Soil Sci. Soc. Am. J. **68**, pp 750-759 (2004).