Implications for Coating of Static and Dynamic Wetting

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Abstract

The static and dynamic wetting of surfaces is central to coating processes. Static wetting controls the extent of spreading on the applicator and substrate, and control of wetting line position is one objective of applicator design. Capillary wicking can cause leakage, and crooked wetting lines can cause coating nonuniformities. In the case of the simultaneous coating of multiple layers, the extent of spreading of one layer upon another must be controlled through the use of surfactants.

Dynamic wetting affects operability limits for coating processes. Most importantly, dynamic wetting failure, the entrainment of air, limits coating speed. Dynamic wetting is strongly influenced by hydrodynamics. However, no experimentally verified physical model exists, and practical knowledge of wetting dynamics has been empirically generated. Dynamic wetting may be controlled through the chemical and physical properties of the substrate and liquid, through flow geometries that provide hydrodynamic assist, and possibly through the introduction of an electromagnetic field.

Introduction

Coating is a process of dynamic wetting because liquid isplaces air from a moving web. Dynamic wetting failure, the entrainment of air, limits coating speed.

Static wetting affects the coating process more subtly. coated width must be controlled, and leakage from the applicator must be avoided. Crooked wetting lines can lead to coating nonuniformities.

Coating flows are of sufficiently small scale that capillary forces are at least as important as viscous, inertial, and gravitational forces. Wetting angles affect meniscus shape that in turn can influence or even control local flow uniformity.

Several detailed reviews of the fundamentals of coating,[1-3] wetting,[4-7] capillary hydrodynamics,[3] and interfacial phenomenally[1] are available. Multilayer coating processes are complicated and require multiple approaches. Detailed physical models can be developed for some aspects of the multilayer coating process. However, complete and verified physical models are not available for other aspects, such as dynamic wetting. For some of the physical models that are established, such as Young's relationship for the static contact angle, either practical conditions violate the underlying assumptions or some of the parameters are not pragmatically determinable. Semiempirical models are useful if some important features can be modeled. When a physical model is unavailable or too complicated, an index measurement of predictive value might be used, or, in the most intractable situations, experimentation using pilot or manufacturing coating equipment.

Because so many aspects of multilayer coating cannot be realistically modeled, a qualitative understanding or extensive empirical knowledge of coating phenomena proves most useful. When the directions for solving coating difficulties are clear, quantification becomes a matter of routine experimentation. This philosophy underlies the following qualitative overview of the connections between wetting phenomena and the coating process.

Multilayer Coating

Color photographic products can comprise 15 or more layers. Economical manufacturing requires that several layers be coated simultaneously. A die with multiple outlets extrudes the layers onto an inclined surface, called a slide, down which they flow by gravity. Each layer flows over that below, and in this way the layers are stacked for coating.

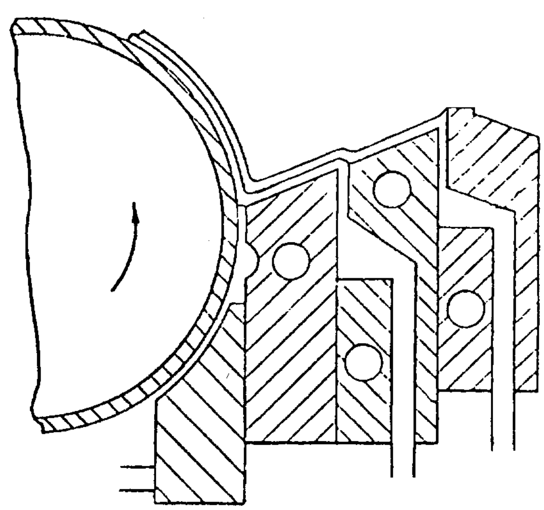

Figure 1: Multilayer bead coating.

In bead coating (Figure 1), the layers span a small gap between the end of the slide and the web on the order of a few hundred microns. A small gap is necessary because it is mainly surface tension that supports the liquid in the gap. A small pressure drop, on the order of millimeters of water pressure, is applied across the gap by means of a baffle under the slide to enable faster and thinner coating than is otherwise possible.

In curtain coating (Figure 2), the layers drop off the end of the slide to form a free falling curtain. The liquid undergoes gravitational acceleration, and the higher impingement speed compared to bead coating enables higher coating speeds. Vertical edge guides maintain the width of the curtain, which otherwise narrows as it falls because of surface tension.

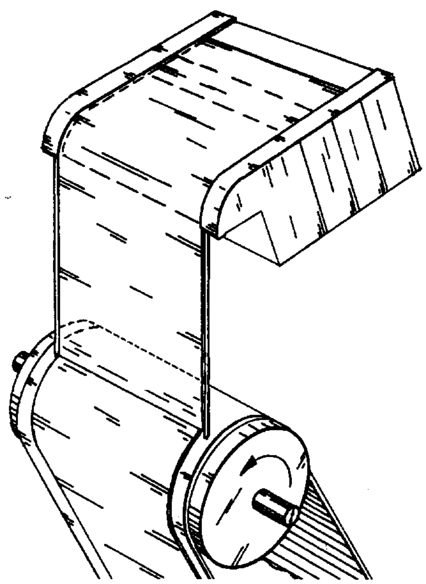

Figure 2: Multilayer curtain coating.

Static Wetting

The wetting of a solid by a liquid at rest is usually characterized by the static contact angle, the angle at which the meniscus intersects the solid surface as measured through the liquid. For conditions of thermodynamic equilibrium and a perfectly flat, homogeneous solid surface, Young's equation uniquely relates the static contact angle to the surface tensions of the interfaces. In practice, however, the underlying assumptions of Young's equation are rarely met, and only the surface tension of the liquid/air interface can be routinely measured, so the contact angle is determined experimentally. With few exceptions, the observed contact angle is not unique.

The range of observed contact angles is called contact-angle hysteresis. Contact-angle hysteresis is generally beneficial to coating because it helps to immobilize the wetting line, which would otherwise be mobile and hard to position. For example, the static meniscus at the edges of a coated film uniquely relates coating thickness to the contact angle; were it not for hysteresis, the edges of coatings would inevitably migrate. Quantifying the extent of hysteresis requires measurement of the advancing and receding contact angles. The advancing angle is the largest contact angle attainable before the wetting line starts moving in the direction of the air phase, and the receding contact angle is the smallest contact angle attainable before the wetting line starts moving in the direction of the liquid phase. Contact-angle hysteresis may be overestimated because the wetting line is moving or because equilibrium has not been attained when the measurement is made.

If the solid has an edge, the wetting line preferentially locates along it. The wetting line remains on an edge for a range of contact angles, given by Gibbs' inequality, that exceeds hysteresis on a flat surface. The sharper the edge, the greater the apparent hysteresis. Edges are frequently exploited in die design to help control wetting line shape and position.

When the advancing contact angle is less than 90°, the liquid is said to wet the solid. If the liquid wets the surface of the die, then it is naturally drawn into cracks and crevices and can migrate over the surface of the die. Leakage and contamination may result. Tightly fitting parts reduce flow rate but do not stem flow (unless flow rate is so low that solidification by drying, gelation, or some other mechanism creates a blockage). Tightly fitting parts can also be expensive and difficult to use and maintain. Capillary wicking can be prevented by making the die from nonwetting material or by treating surfaces to be nonwetting, although surface contamination may defeat such an approach. Capillary breaks can be designed into hardware to halt spreading. The geometry of a capillary break is such that the meniscus achieves an equilibrium configuration, and the liquid progresses no farther.

Meniscus Shape and Flow Uniformity

The shape of the meniscus may be either a hydrostatic shape imposed on the flow or a dynamic shape coupled to the flow. Either way, the contact angle at the edges of the meniscus affects meniscus shape, and meniscus shape in turn affects flow distribution. Solving the Young-Laplace equation for the shape of a static meniscus and then computing the flow distribution is usually manageable, but flow with a dynamic meniscus requires solving the more complex equations of capillary hydrodynamics. Whether by computation or by observation, wetting conditions at the edges of the liquid are found to affect local coating uniformity strongly.

Figure 3 shows a cross section of the slide near an edge. The rectangular sidewall shown is just one possible edge geometry, and the wetting line is presumed pinned on an edge. Fully developed flow, approached with distance down the slide, is normal to the plane of the drawing; viscous drag from the solid boundaries balances the gravitational force parallel to the slide. The meniscus is a static meniscus with a hydrostatic pressure field determined by the component of gravity normal to the surface of the slide. The flow distribution adapts to this shape, as shown qualitatively in Figure 3; except near the sidewall, the flow rate increases with local film thickness.

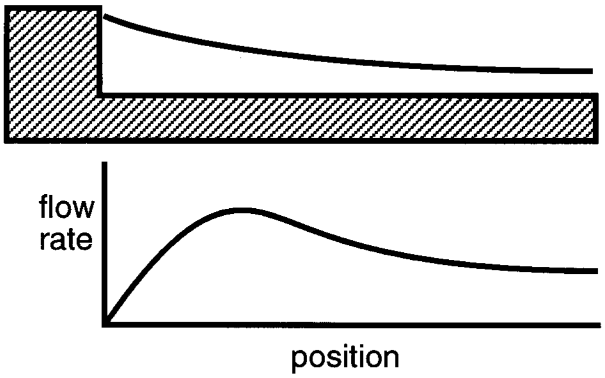

Figure 3: The meniscus at the edges of the slide controls the local flow-rate distribution .

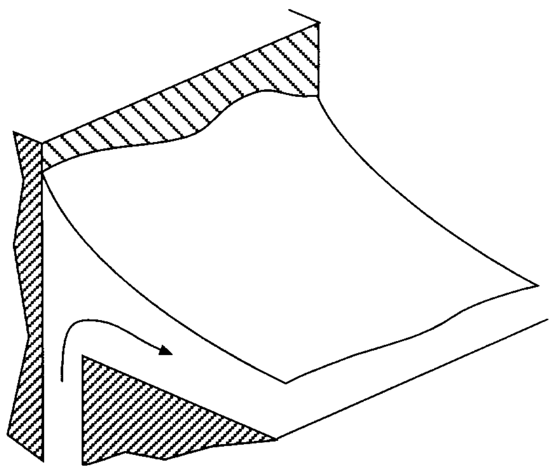

Figure 4: An irregular wetting line can distort meniscus shape and redistribute flow.

Figure 4 shows the meniscus at the top outlet on the slide; the high backwall is just one possibility for the geometry. The wetting line shown is crooked. Hysteresis enables the contact angle to vary with position, and any number of meniscus shapes may be possible. The history of the process may have to be managed to obtain the desired shape repeatably.

The irregularities in the wetting line affect meniscus shape, which in turn influences the flow distribution. Leveling driven by gravity and surface tension flattens the meniscus and smoothes the flow distribution with distance down the slide. If the slide is sufficiently long, the influence of the irregular wetting line on the flow distribution is lost.

However, leveling that is incomplete where the next layer issues onto the slide will continue and affect the flow distribution in both layers. Ultimately the air interface flattens, but the dividing surface between the layers does not (Figure 5). The layers are usually not separate phases, and so there is no interfacial tension. Moreover, the density difference between layers is small compared to that between liquid and air, and the denser liquid may even be on top. So, the nonuniformity in flow rate resulting from the irregular wetting line becomes permanent, and a coating nonuniformity results.

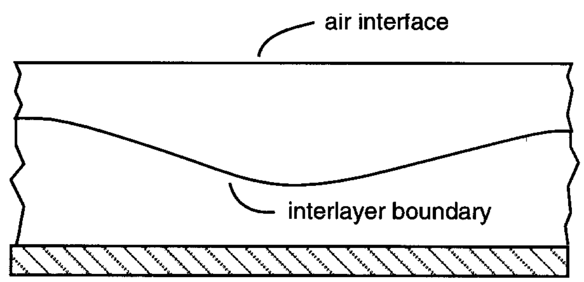

Figure 5: Surface tension and gravity act to flatten the air interface, but there is little or no tendency for the boundaries between layers to flatten.

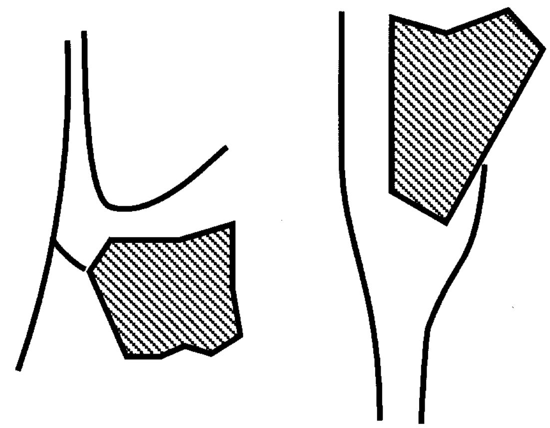

Figure 6: The wetting line at the lip affects flow in all the stacked layers.

On the slide, there may be a significant distance between the wetting line and the subsequent outlet so that smoothing of the flow distribution can occur, but at the die lip the wetting line is close to all layers (Figure 6). Consequently, a crooked wetting line can disrupt the flow-rate distribution in every layer. The air interface on the coated web may flatten before drying, but the dividing surfaces between layers remain distorted.

Effect of an Electrostatic Field

If a web that is electrically insulating is placed on a conductive solid, and if a steady or oscillating voltage is applied to the solid, then an electric field is created above the web. The contact angle of a liquid placed on the web decreases as the voltage is increased. The field creates a force that reduces the contact angle and advances the wetting line[12,13]; typical data are shown in Figure 7.

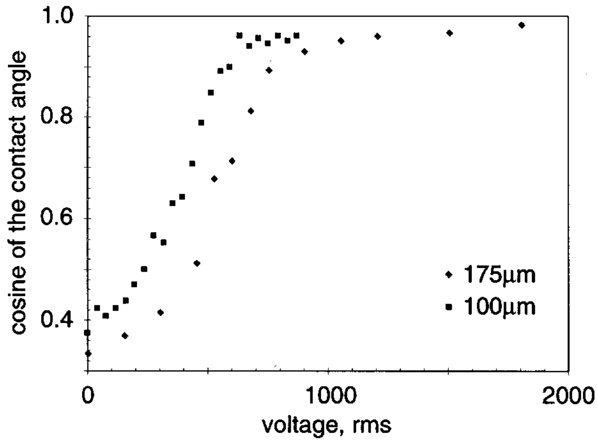

Figure 7. Data by A. Clarke for the effect of an electrostatic field on the contact angle of water on poly(ethylene tere-phthalate) web of two different thicknesses.

Layer Spreading on the Slide

Control of static wetting also ensures that the layers completely blanket each other. One layer spreads over another if it has the lower surface tension. If the top layer has the higher surface tension, its interface contracts and drags the underlying liquids with it.

The complication in applying this ostensibly simple spreading criterion is knowing the values of surface tension. Surface tension level is controlled by adding one or more surfactants. In addition, the layers nearly always contain surface-active components, as well as emulsions and dispersions that interact with surfactants. It takes time for surfactants to diffuse to the air interface and adsorb there. So, the surface tension at an air interface depends on time or position.

When layers are stacked, an underlying layer may become exposed to air at an edge (Figure 8). The top layer has the older surface, and so it has an inherent advantage for having a surface tension lower than any exposed underlayer. Nevertheless, because the underlayers may contain high levels of surfactants, an adverse outcome is possible. The measurement of surface tension on a slide is feasible if not easy.

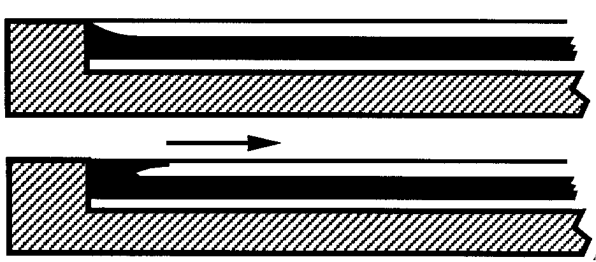

Figure 8: The top layer contracts if an exposed underlayer has the lower surface tension.

Alternatively, surface age on a slide can be estimated and matched to a dynamic-surface-tension measurement.

Dynamic Wetting

Wetting is dynamic if the contact line is moving. At imperceptible speeds, dynamic wetting limits to static, equilibrium wetting. The contact angle changes with the speed of the wetting line and so is called a dynamic contact angle. The dynamic contact angle is not a material property and does not have the fundamental significance and general applicability of the static contact angle. At typical coating speeds, dynamic wetting may be a nonequilibrium rate process influenced by hydrodynamics.

The dynamic contact angle most often increases with speed. Air is entrained as it nears its maximum possible value of 180°. A shallow approach of the meniscus to the web creates high pressure in the air through the lubrication effect. Thus the air, even though its density is one-thousandth that of a liquid and its viscosity less than one-hundredth, can penetrate between the liquid and the web and disrupt the flow.

Besides air entrainment, the dynamic contact angle affects coating uniformity if it varies with time or position because of variations in the web. Beyond that, its value affects the position of coating boundaries; the level of vacuum assist required for bead coating is an example.

Factors Affecting Dynamic Wetting

High coating speeds are favored by factors that decrease the dynamic contact angle, and these are not always the same as those that decrease the static contact angle. Perhaps the most important factor for coating is viscosity, because its value can vary by orders of magnitude. Generally the dynamic contact angle decreases, and the speed to air entrainment increases, as viscosity is lowered. A low viscosity for the purpose of dynamic wetting can also be achieved with a higher viscosity, shear-thinning liquid because shear rates near the moving web are high, 10^6 reciprocal seconds or higher. That viscosity should be a controlling variable is indicative of the different natures of dynamic and static wetting.

Figure 9 shows typical results for the effect of viscosity on maximum wetting speed for a tape plunging vertically into a pool. On a logarithmic plot, the data fall on a straight line. Such data show trends but are not directly predictive of the maximum speeds of coating processes.

Figure 10 shows dynamic contact angle data for aqueous glycerol, a Newtonian liquid, and aqueous poly(vinylpyrrolidone), a shear-thinning liquid. Although both liquids have the same viscosity at low shear rates, the shear-thinning liquid attains a much higher speed before dynamic wetting failure because its effective viscosity at the dynamic wetting line is far below its nominal viscosity.

A high surface tension for the liquid favors dynamic wetting; this trend is opposite that for static wetting. The chemical properties of the support are also important, but the value of the static contact angle does not correlate directly with maximum coating speed. In particular, a small contact angle does not necessarily portend high coating speed.

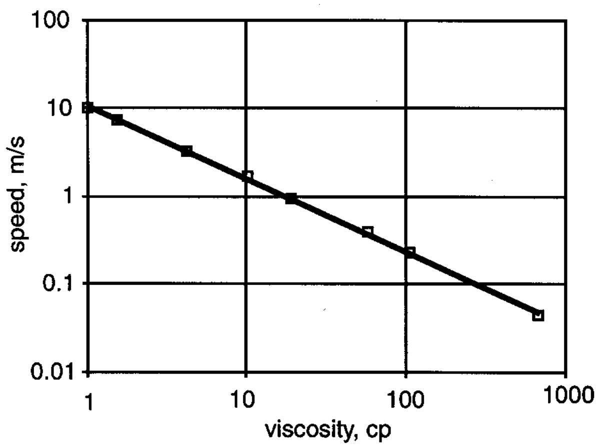

Figure 9. The speed of dynamic wetting failure versus vis-cosity for a poly(ethylene terephthalate) web plunging into a pool of aqueous glycerol .

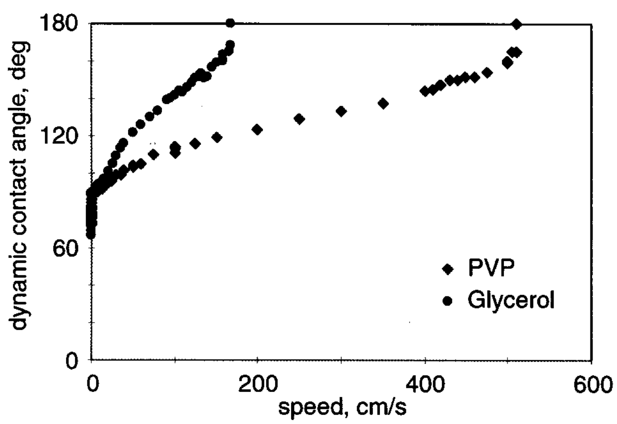

Figure 10: Dynamic contact angle versus speed for poly(ethylene terephthalate) web plunging vertically into two liquids, aqueous glycerol and poly(vinylpyrrolidone), with nominal viscosities of 10 cp.

Increased impingement speed favors increased air entrainment speeds. In curtain coating, curtain height enables high viscosity liquids to be coated at speeds characteristic of low viscosity liquids in bead coating, as Figure 11 demonstrates.

Figure 11 also shows that air-entrainment speed is a strong function of flow rate. At very low flow rates, air can be entrained by webs that are barely moving. The importance of flow rate is again suggestive of hydrodynamic influences on dynamic wetting.

At first glance, it might appear that surface roughness should always decrease the air entrainment speed, since the wetting line must move a greater distance over a rough surface than over a flat one of the same nominal area. Roughness might also be expected to increase viscous dissipation and so increase the dynamic contact angle. On the other hand, small, residual pockets of air might not be detected and may reduce the drag of the web on the liquid. A sufficiently rough web can alter the entire flow field and indirectly influence dynamic wetting. Even the directional impact of roughness is difficult to anticipate, and experimentation is necessary.

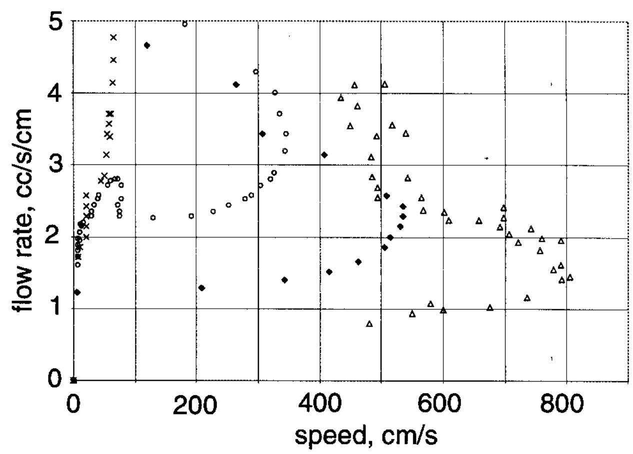

Figure 11. Data by T. Blake and D. Morley for air entrainment speeds for the curtain coating of 15% bone gelatin, having a viscosity of 63 cp, on gelatin-subbed poly(ethylene terephthalate) web. From left to right on the graph, the data sets correspond to heights of 1, 2, 6 and 25 cm; curtain impingement is normal to the web.

The dynamic contact angle, as well as the static contact angle, is reduced by the application of an electric field. At the coating point, the potential of the roller can be maintained at several hundred volts with respect to ground potential to create a field that attracts the grounded liquid. Alternatively, the surfaces of the web can be charged before the coating point much as a capacitor. Opposite charges on opposite sides of the web create an electric field within the web. When one side of the web is grounded by a roller, the charge on that side of the web is neutralized, and the charge on the other side of the web creates an electric field that attracts the grounded liquid.

A nonuniform field causes variations in the dynamic contact angle, and the variation in the dynamic contact angle distorts the dynamic wetting line. Coating nonuniformities are produced just as for a crooked static wetting line at the die lip. So, although an electric field increases coating speeds, it can also degrade coating uniformity if it varies with time or position. The unwinding and conveyance of the web creates charges, so the control of charges on the surfaces of the web is necessary whether or not an electric field is used to assist dynamic wetting.

Acknowledgments

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