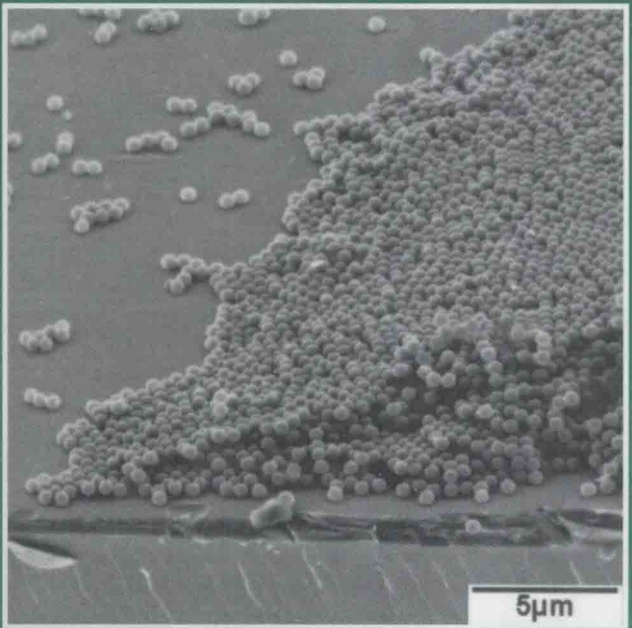
ACS SYMPOSIUM SERIES 790

Film Formation in Coatings

Mechanisms, Properties, and Morphology



EDITED BY

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Film Formation in Coatings

Mechanisms, Properties, and Morphology

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Foreword

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Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

ACS Books Department

Preface

Coatings technologies are still heavily influenced by the "Clean Air Act" of 1990 and its subsequent updates that keep reducing the volatile organic content (VOC) of coatings. The continuing development of high solids, powder, waterborne and radiation-curable coating technologies is highly focused on reducing the emission of VOCs while maintaining and/or improving product properties in a cost-effective manner. Understanding the film formation process is one of the key enablers in the further development of these coatings technologies. This understanding involves continued elucidation of film formation mechanisms, the evolution of film properties during film formation, and the resultant morphology and structure of the films. The film formation knowledge base continues to grow facilitated by advances in instrumentation that has been applied to this area of investigation, as well as progress made in modeling various aspects of the film formation process.

The first section of this book focuses on aspects of the mechanism of film formation including the modeling of drying of polymer colloids, modeling and understanding capillary forces and stress involved in drying latex coatings, and understanding the effect of molecular weight and molecular interactions on film formation. Instrumental methods such as fluorescence decay spectroscopy, Fourier transform infrared spectroscopy (attenuated total reflectance and photoacoustic), atomic force microscopy (AFM), ellipsometry, and thermogravimetric analysis have contributed to our understanding of various aspects of film formation. The second section focuses on film properties developed during the film formation process for waterborne thermoplastic and cross-linkable systems as well as radiation curable systems. The focus on property development in this section involves the use of dynamic mechanical analysis, dielectric spectroscopy, and swelling measurements. The third section focuses on the morphology and film structure resulting from the film formation process. This is a very active area of study utilizing advanced morphological instrumentation, such as transmission electron microscopy, cryogenic scanning electron microscopy (SEM), confocal microscopy, environmental SEM, AFM, as well as routine measurements of gloss and film porosity. The instrumentation used in these studies also facilitates the determination of unique and novel film structures in some of these studies.

We hope this book will encourage and foster continued studies to further our understanding of the scientifically challenging and commercially relevant issue of film formation in waterborne coatings.

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Chapter 1

Drying Modes of Polymer Colloids

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This chapter reviews the complex step of drying in the latex film formation process. Drying modes have a profound effect on drying rates and on the final properties of films, primarily through their influence on film morphology and the distribution of water-soluble species. Three distinct drying modes (acting separately, successively or together) can be defined, namely *homogeneous drying* (in which the water concentration remains uniform in the sample throughout the drying process), *drying normal to the surface* (where a dry layer of increasing thickness develops from the air surface of the latex coating); and *lateral drying* (where dry areas increase in size in a direction parallel to the substrate). Details are given on the current knowledge and understanding of these drying modes. The last section of the chapter considers the main parameters controlling the drying modes, i.e. thickness and geometric effects, the structure and rheology of the dispersion, particle viscoelasticity, and the overall rate of water loss.

Environmental and health regulations are causing the manufacturers of coatings and paints to develop new formulations. One important strategy for coatings that are friendly to the environment is based on waterborne colloidal dispersions of polymers. As industry is confronted with the need to replace coatings formulated in organic solvents, more coatings are converted from being based on polymers dissolved in solvent to those based on colloidal dispersions in water. This is the reason why waterborne film formation mechanisms are becoming increasingly important and relevant to product design. A number of useful reviews of latex film formation have recently been published (*1*, *2*, *3*). The film formation process is commonly divided into 3 steps. As water evaporates from the dispersion, the polymer particles become more and more concentrated and come into proximity (step 1). When the forces accompanying drying exceed the mechanical (both elastic and viscous) resistance of the particles, particle deformation occurs to yield a void free film that is still mechanically weak (step 2). In the final stage of film formation, polymer diffusion occurs across the interparticle boundaries to provide the entanglements that give strength to the film (step 3). These steps are not always well separated, and within each step subtle features operate that often differ from system to system. In certain cases, additional steps can be observed in the film formation process. Some factors (such as uniform particle size and low ionic strength) promote ordering of the dispersion in the liquid state. The disorder to order transition can be considered as an additional step (*4*). Furthermore, all latex particles have surface polar or ionic groups that provide colloidal stability. In some systems, this polar layer is sufficiently thick that it forms a continuous phase called a membrane in the freshly formed film (*5*). Break-up of this membrane becomes an important step in bringing the particles cores into intimate contact so that interdiffusion can occur (*6*).

This chapter focuses on the drying modes of polymer colloids. Drying encompasses step 1 and part of step 2 in the above description of the latex film formation. The mechanism of water loss from latex dispersions is surprisingly complex. This stage of film formation is, at present, the least understood (*1*).

Drying modes are very important for several reasons. They determine drying rates which are of technological importance. Perhaps the most important example of the need for rapid drying, which to our knowledge has not been described at all in the open literature, is waterborne road paints. These paints must dry within minutes of application to a road surface so that the painting process does not impede traffic. For some other applications, one would like to slow down the drying process to increase the "open time." The open time is the time available for the "touch up" of flaws in a coating to be made without permanent disturbance of the surface. Once the open time is over, the surface cannot be "re-worked" or smoothed out. Solvent borne paints normally have much longer open times than waterborne paints. The classic example involves alkyd coatings. Solvent borne alkyd coatings have long open times whereas water-borne emulsified alkyd resins are much more difficult to rework (*7*). We lack a mechanistic understanding of the factors that control open time. However, the viscosity of the formulation is likely to play an important role. The viscosity of polymer solutions increases monotonically as the solvent evaporates and the polymer becomes more concentrated. Polymer molecular weight has a large effect on the solution viscosity. In colloidal dispersions, the viscosity is low at modest concentrations, but rises abruptly as the solids content reaches values above 55 to 65 vol %, depending upon the size distribution of the particles. Above a critical value of viscosity, the surface cannot be smoothed out, but more important, addition of fresh coating at lower solids content may not be able to redisperse latex particles which have coalesced on the substrate. Furthermore, the user of a paint judges the "amount of dryness" by examining the air surface. It is the viscosity at the surface of a coating that most heavily influences perceptions of open time. The distribution of water within a layer, and not the overall average water concentration, is thus the more important parameter. The exact drying mode will determine the distribution of water within a drying layer, and so theoretical and experimental investigations of drying are certainly warranted.

Another important issue is that drying implies transport of water in the latex dispersion. This transport can involve diffusion of water molecules through a continuous polymer phase, percolation of water through interstitial spaces in the film, or water fluxes in the wet regions of the drying film. The fluxes are particularly interesting because they can transport polymer particles, pigment, and water-soluble species from wet regions to the boundary to adjacent dry regions of the film. Transport of particles will influence the array of particles and thus the morphology of the film. On the other hand, transport of water-soluble species, such as surfactants or soluble oligomers, will influence the final distribution of such species in the dry film (*8*). Both the morphology and the distribution of water-soluble species have a profound influence on the properties of latex films.

From a phenomenological point of view, one can distinguish three distinct drying modes (and these can act separately or together) for a latex dispersion on a non porous solid substrate. Depending on the authors, they are referred to by different terms. Therefore, let us first clarify the vocabulary. The first mode is *homogeneous drying*. This means that the water concentration remains uniform in the system throughout the drying process. The tendency to dry homogeneously is very general. All drying systems tend to compensate for heterogeneous water concentrations. Dilute latices start drying homogeneously. However, once a certain solids content has been reached, which depends on the particular system and drying conditions, heterogeneities in the distribution of water can appear. Heterogeneities occur when the rate of water loss is too high, and the equilibration of water inside of the system does not have time to take place. Examples of real homogeneous drying in latex dispersions, in which homogeneity is retained throughout the drying process, are very rare and this case will not be developed much in the following text.

The second mode is *drying normal to the latex dispersion surface*. In this case, the heterogeneity in the distribution of water is such that the top of the latex coating (the air side) is drier than the bottom, on the substrate side. Drying proceeds by a movement in a direction normal to the surface of a drying front separating a top dry region from a bottom wet region. Systems drying like this, in which the dry region undergoes particle coalescence, are sometimes called "skin forming systems".

Drying fronts can also propagate in a lateral direction, parallel to the substrate. This mode is called *lateral drying*. Very often drying occurs inward from the outer edges and thus the center of the specimen is the last region to dry. This final region to dry has been called the "last drop". It can have special characteristics, such as high concentration of water-soluble species and special morphology, as has been found recently (*9*). Later in this chapter, we will mention factors, such as the addition of thickeners or high-solids dispersion (both of which raise the dispersion viscosity), which are expected to suppress lateral drying. Normal and lateral drying modes are depicted in Figure 1.

This chapter will consider four main topics: normal drying; lateral drying; mixed modes of drying; and in the final section, the parameters that determine the drying modes.

Drying Normal to the Surface

When a latex dispersion dries normal to the surface, a dry layer of increasing thickness builds up from the top downwards. Water has to diffuse through this top layer in order to leave the film. If the diffusion through this layer is the slow step in the drying process, then the drying rate is not constant, but it decreases progressively. If the water content in the film is plotted versus the square root of time, a straight line is obtained, the slope of which can be related to the diffusion coefficient of water through the dry top layer (*10*). An example of this behavior was found in the case of the drying of a concentrated (84 wt% solids), reactive (crosslinking upon drying), polydimethylsiloxane emulsion (*11*). However, diffusion through the top layer is not always a slow step and the global rate of water loss can be constant over a large period of time in normal drying (*12*).(By global, we mean the overall rate, as compared to the water loss rate in a local region within the coating.) It is the tendency of the system to equilibrate the concentration of water between the top and the bottom which drives water from the bottom to the top and is responsible for the drying of the whole film.

A possible consequence of this mode is that water soluble species, which tend to remain in water as much as possible, are driven to the film-substrate interface. Accumulation of such species, like surfactants, at this interface can strongly affect the properties of the film, especially adhesion (*13*). In studies of the distribution of surfactants in latex films by Urban and coworkers (*14*) and Holl and coworkers (*15*), such a mode is invoked to explain the high concentration of surfactants often observed at the film/substrate interface. However, in certain cases, more subtle transport mechanisms for surfactants have to be taken into account like osmotic and capillary pressure gradients occurring near the interface (*11*).

Classical Models for Normal Drying

Traditional models for the drying process are based upon measurements of the rate of water loss from latex dispersions. Almost all the experiments on which the classical models were based involve dispersions stabilized by surfactants. Water

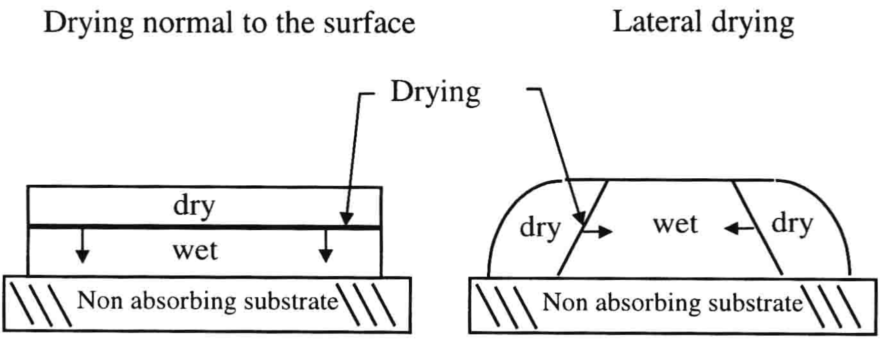

Figure 1 : Schematic diagram showing two possible drying modes for latices, namely normal and lateral drying.

is lost initially at a constant rate, and then the rate slows down until water loss is complete. The three main models are due to Sheetz (*16*), Vanderhoff (*17*), and Croll (*12*, *18*).

Sheetz 1965

Sheetz (*16*) proposed that very early in the drying process, a dry skin of coalesced particles forms on top of the latex dispersion. Further evaporation of water then occurs by diffusion through this skin. In fact, the main emphasis of his work was not drying modes but particle deformation. He made an analogy to a piston in which the coalesced surface layer exerts pressure on the wet layer underneath. His work was primarily theoretical, based on his limited experimental study of acrylic latices.

Vanderhoff 1973

In Vanderhoff *et al.*'s model (*17*), drying is described as a three stage process. In stage 1, water evaporates at its normal rate from the surface of the dilute dispersion, in which the particles remain separated. Stage 2 commences as the particles come into close contact and protrude at the latex dispersion-air interface. As the area of the water-air interface is reduced, the evaporation rate slows. Eventually, coalescence leads to the closing of the surface. In stage 3, the loss of the last traces of water is very slow because the water now must diffuse through a layer comprising continuous polymer at the surface. This last suggestion may be correct under certain circumstances. For example, there is some evidence that near the end of the drying process, the rate of water loss is consistent with Fickian diffusion of water through the solid polymer (*19*, *20*, *21*). On the other hand, when the latex particles have sufficient polar material in their shell that it forms a continuous hydrophilic phase in the film as it dries, water diffusion through this phase may be the most favorable route and may predominate.

This model has an appealing simplicity and had a strong influence on many researchers over the years. However, it made an implicit claim for generality which is unjustified as it is obviously not applicable in the most frequent cases of lateral drying.

Croll 1986

Croll (*12*, *18*) conducted one of the more significant experimental and theoretical works on the topic of latex dispersion drying. Based on his experimental work, he proposed a two-stage process, unlike Vanderhoff *et al.* 's three stage model. He compared the rate of water evaporation from latex dispersions to that of pigment suspensions (clay, mica) where coalescence is not possible, and found remarkable similarities. Both the latex dispersions and the pigment suspensions exhibited a loss of water that was linear with time over much of the drying process, independent of film thickness, and in each instance, this rate was 85% of that of water itself. In the first stage of this model, particles form a flocculated phase at the air interface. The surface from which water evaporates recedes into this phase, leaving a dry porous layer. This phase is initially thin and becomes thicker as the drying proceeds. Beneath the evaporative surface is a "transition layer" of closely packed particles immersed in water on top of a liquid phase containing mobile particles. Croll describes the dry top phase in terms of a percolation network of voids which permits water vapor to pass. Since the top layer does not constitute a real barrier to the transport of water vapor, the rate of water loss is constant during the first stage, whatever the thickness of the layer. The second stage starts when the water evaporation rate begins to slow down. This corresponds to the time where the transition layer reaches the substrate and the concentration of water in the wet region decreases. Then, the flux of evaporating water decreases eventually to zero. In a subsequent paper (*18*), Croll developed a mathematical model to describe drying during latex film formation with an emphasis on thermal aspects of the drying process which had not been previously investigated much in the literature. He considered the temperature decrease due to the endothermic drying process, which in turn decreases the drying rate. His model made use of values of thermal conductivity, thermal expansivity and viscosity of the latex dispersion. Croll's model is then more quantitative than Vanderhoff *et al.*'s one but has the same drawback: it is not general as it does not account for lateral drying. This model, slightly modified, was used by Eckersley and Rudin (*20*) to fit their results on skin forming systems.

Whereas the above models for normal drying capture certain features of the drying process, they are neither general nor complete. In the last section of this chapter, we will review recent ideas used to predict when normal drying will occur. Let us now discuss the case of lateral drying.

Lateral Drying

Lateral drying, as defined in the introduction of this chapter, was observed and reported in the literature a long time ago. In 1964, Hwa (*22*) reported lateral nonuniformity during the drying of a film forming acrylic latex dispersion. He observed three regions with different appearances: a central wet region that was turbid; a peripheral dry region that was optically clear; and a region between the other two that was partly cloudy. The central turbid region decreased in area as drying proceeded. Hwa proposed that the intermediate region consisted of flocculated particles that could not be redispersed in water. In the same year, Myers and Schultz (*23*) published ultrasonic measurements of the lateral drying of latex films. Okubo *et al.* (*24*) constructed a description of drying similar to that of Hwa, with the additional observation of a skin forming on top of the central wet region. We will comment further on this work by Okubo *et al.* later in the chapter.

More recently, Chevalier *et al.* (*5*) followed the drying of latex dispersions using Small Angle Neutron Scattering. The particular latex dispersion studied had a hydrophobic core with a hydrophilic shell. They found that the spacing of particles in the central wet region of a drying film remained roughly constant, even though the global volume fraction of polymer, Φ, increased because of water evaporation. At a particular point in time, the spacing of the particles decreased abruptly and Φ approached 1. They associated this collapse with the passing of a "coalescence front" through the spot being irradiated by the neutron beam. They postulated that a coalescence front moved inward from the edges by the action of the particles in the central wet region colliding with and sticking to it. Even though it was proposed that particles were transported from the central regions outward toward the edges, Φ stayed roughly constant because of evaporative loss of water. This concept of a central region with a constant polymer concentration is incorporated into the so-called "shape models" of drying that will be discussed in the next section.

In some ways, this work of Chevalier *et al.* describes the same process observed by Hwa (*22*) and like the work of Okubo *et al.* (*24*), it shows that the water content in the central wet region remains high, but it is low in the flocculated and dry regions. Somewhat earlier, the same group (*4*) had also observed a dry region surrounding a central wet region in a surfactant containing latex dispersion during drying. They found as evaporation proceeded that the central region increased in thickness and decreased in surface area. They suggested a different mechanism in which "water is expelled from the drying film into the wet area". This later view of water expelled from a water-poor region into a water-rich region is inconsistent with the predictions of thermodynamics but can have some equivalence in phase separation phenomena occurring in emulsions. However, to our knowledge, this idea was never developed any further in the literature.

It is surprising to note that lateral drying was observed by researchers like Sheetz (*16*) and Croll (*12*) who did not take it into account in their models. Interestingly, Croll attributed the observation of latex films becoming optically clear near their edges first to the belief that air was drier there and allowed faster evaporation. Another possible explanation will be presented in the next section. Nevertheless, some authors (*25*) still use Croll's normal drying model or the version modified by Eckersley and Rudin (*20*) to fit their drying data even when they observe lateral drying (*26*).

General Considerations about Lateral Drying

In almost all observed cases of lateral drying in laboratory specimens (in which there is a convex shape of the dispersion layer), drying fronts move inward (from the edges toward the center). The opposite case also exists (drying from the center toward the edges) but only when the thickness of the central region is initially thinner. In the following, lateral drying will be considered as occurring from the edges inward.

Lateral Transport of Water

All authors who have studied lateral drying have come to the conclusion that when a latex dispersion dries laterally, water moves in a lateral direction, i.e. parallel to the interface with the substrate. The problem is often discussed by considering the drying of drops of aqueous dispersions on solid non absorbing substrates since this situation neatly encapsulates many of the open questions. Two possible causes of lateral transport of water have been proposed.

One is based on the fact that at the beginning of the drying process, in a convex drop of emulsion, even if the water concentration is constant over all of the volume, the absolute amount of water is lower near the edges where the drop is thin than in the center where it is thick. If the water evaporation rate is uniform across the surface (neglecting effects of surface curvature), the water will be depleted first near the edges. Soon, a gradient of concentration of water appears oriented from the central part of the drop towards the edges. This lateral gradient will subsequently cause a diffusive flux of water from regions of high concentration to low concentration. The same argument holds for initial shapes other than drops. Large planar films have edges often thinner than the central part, and at these edges, the time for full drying is expected to be shorter. Even in the coating of very large areas, there are usually regions of thinner application, such as caused by brush strokes. As there will almost always be thinner regions in a wet coating, lateral transport of water is usually relevant in the drying process.

Another possible cause of lateral transport of water is the fact that the convex drop tries to maintain a particular shape. One assumes a dominance of surface energies in determining the drop profile. First, the drop keeps the shape of a spherical cap because of its surface tension. Second, at the edges, the drop can either retain a constant contact angle or a constant base (more details will be given later). With uniform evaporation of the drop at the air-liquid interface, the relative change in drop height is greatest at the thin edges, and the flow (from the center to the edges) seeks to rectify the consequent shape changes. These kind of shape