Film Formation from Latex Dispersions

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The dominant, capillary forces operative in film formation of latex dispersions, and how theoretical models have dealt with them over the years are addressed. The force by the receding water surface is the dominant driving force. Capillary liquid bridge forces are less effective. Environmental relative humidity (RH) virtually does not influence these forces. With a light transmission technique, the effect of temperature and humidity on the film formation of a surfactant-free butyl acrylate latex was studied. Film formation is successful at temperatures higher than a value slightly below T_g. RH only slightly promotes film formation, presumably because water acts as a solvent. Also, the film promoting action of normal cosolvents as a function of concentration was clearly demonstrated.

INTRODUCTION

A trend to replace conventional solvent-based coatings with waterborne ones is apparent. In general, those waterborne coatings consist of pigment (e.g., TiO_2), polymer particles (binder), water (solvent), and additives (thickeners, dispersants, anti-foam agents, etc.). The film formation proceeds while the water evaporates. When the temperature is sufficiently high, the film formation will be successful. A considerable number of authors have described this process theoretically. These studies have been reviewed by Visschers et al.[1]

In this paper we discuss which of the operative forces in film formation are the dominant ones. The prevailing forces are evaluated in more detail. We briefly indicate the evolution of theories over the years. Also, the influence of material parameters (particle size, wetting properties, etc.) and drying conditions (temperature, humidity, etc.) are discussed. Then, an experimental film-drying cell as well as the results obtained are presented. Other potential applications to investigate the performance of waterborne paints are discussed.

THEORY OF FILM FORMATION

Forces Involved in Film Drying

If one applies a latex onto a substrate and subsequently dries it below a certain temperature, the resulting film will consist of a nontransparent, powdery film. This opacity indicates that there are many residual voids left within the film that are capable of scattering incident light. However, if one dries the latex above this temperature, the result will be a homogeneous, transparent film. This apparent critical temperature is called the minimum film forming temperature (MFFT). Since there is virtually complete water evaporation in both cases, the existence of the MFFT indicates that, apart from the evaporation of water, another process is involved in film formation: the spherical polymer particles deform to dodecahedra touching each other, leading to the disappearance of boundaries within the film. This process evidently is driven by a reduction of the interfacial energy and is called coalescence. It is depicted in *Figure* 1.

In a drying suspension of polymeric binder particles, a variety of colloidal forces are operative. Neglecting hydrodynamic forces induced by convective or diffusive water movement to the film surface, the operative forces are shown in *Figure* 2. Of these forces, only the Coulomb and the deformation forces are repulsive, the others are attractive. These forces have been discussed in detail by M. Visschers et al.[1] Typical magnitudes of these forces are given in *Table* 1. From this table, it is evident that the capillary and the deformation forces are the prevailing ones. These will be addressed in the next subsection. Note that capillary forces are only effective in film formation when the binder is a

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surface for which water is a wetting agent (contact angle $\theta<90°$). In a separate paper, we demonstrated that this is the case, even for the relatively hydrophobic polystyrene latex in the absence of surfactants.[2]

Dominant Forces in Binder Film Formation[1,3]

In 1951, Dillon et al.[4] published one of the first papers on film formation with latex particles. They supposed the particles to sinter in the absence of water and considered the driving force to be entirely due to the polymer/air interfacial tension (γ_{pa}). The nature of the resistance to deformation was supposed to be purely viscous. The deformation-time dependence expected was confirmed by experiments with drying latex (i.e., in the presence of water).

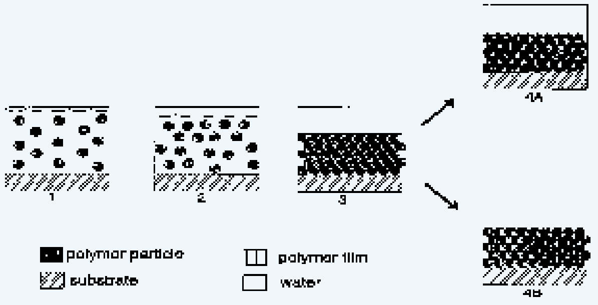

Figure 1—Drying of latex film beyond (route A) and below T_g (route B).

Table1—Typical Values for Operative Forces During Drying of Binder Films. Particle Radius r_p: 250 nm; Hamaker Constant: 1.05 10^{-20} J; Electrical Surface Potential: -20 mV; Salt Level: 1 mM; Surface Tension of Water: 70 mN/m; Contact angle: 0°; Polymer Modulus: 10^7 N/m^2.

Type of Force	Estimated Force / N
Gravitational	$6.4\ 10^{-17}$
Van der Waals (hard spheres)	$5.5\ 10^{-12}$
Electrostatic	$2.8\ 10^{-10}$
Capillary (receding W/A interface)	$2.6\ 10^{-7}$
Capillary (liquid bridges)	$1.1\ 10^{-7}$
Elastic deformation	$1.0\ 10^{-7}$

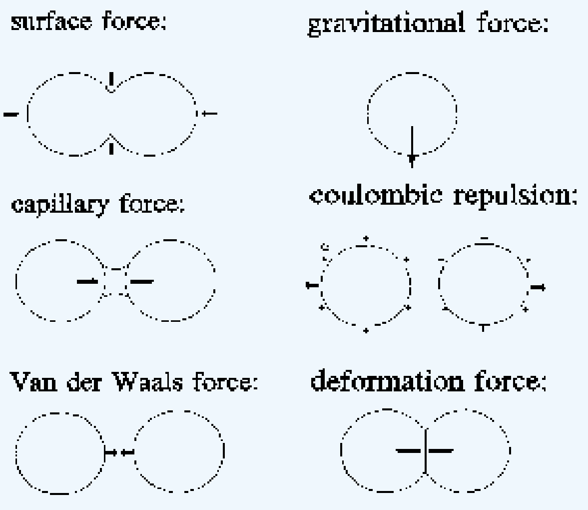

Figure 2—Operative forces in binder film formation.

Brown[5] pointed to the importance of the water/air interface receding during the drying process. He supported this with the experimental finding that, beyond the MFFT, a wet stacking of latex particles shows a much faster film formation than a dry stack of particles. As a resistance to particle deformation, he used the elastic modulus of the particles that he supposed to be purely elastic. He showed that the surface tension of water (γ_{wa}) was responsible for the particle deformation encountered. The effect of the MFFT was explained by the large jump in modulus of the polymer particles at the glass temperature T_g. Later, Sperry et al.[6] showed that a latex dispersion from which the water had previously been removed below T_g (resulting in a powdery opaque film), showed a (very slow) gain in transparency when heated beyond T_g.. This indicates that γ_{pa} may still play a role.

In accordance, Brown developed a theoretical model in which the capillary forces and the elastic-mechanical forces balance. The mechanical force was taken from the Hertz theory[7] for elastic contacts. The capillary pressure originates from the rather basic physical notion (Laplace's law) that a pressure difference should exist over a curved interface (see *Figure* 3). The capillary pressure was taken from the largest curvature of the meniscus in a receding interface. In converting this to a capillary force, an inaccuracy in defining the representative cross-sectional area of the particles was later corrected by Mason.[8] Mason's theory predicts a capillary force on an individual particle that gradually drops with progress of deformation of the particle. This is plotted as the lower line in *Figure* 4 (the upper line shows an improved result by the present authors, which not only accounts for the Laplace pressure but also for the direct surface line tensions[3]). In this graph, successful deformation (homogeneous film without voids) is realized at an "extent of deformation" of 0.95.

As with progressive deformation, the contact area between the particles increases, the resultant stress induced in the particle (~force/area) drops down even more. Thus, not all films that start to deform by capillary forces will necessarily achieve the state of successful deformation. The final result of Mason's analysis is that successful deformation will occur if

$$G < 266\frac{\gamma_{wa}}{r_p}$$

where G is the shear modulus of the binder medium and r_p is the radius of the binder particles. Although experience indicates that successful film formation is promoted by employment of small latex particles, until now the predicted $G \sim r_p^{-1}$ relationship has not been corroborated by experiments (see, e.g., Rudin et al.[9]).

Lamprecht[10] extended the elastic material response to a linear viscoelastic one. He also corrected a flaw in a prefactor as produced by Brown and Mason. His approach, which implicitly contains a rate dependent resistance, would also allow the prediction of the speed of film formation. A point that has not been resolved until now is that the deformation of the particles is too large to assume linearity of the viscoelastic material properties.

A completely different approach was followed by Kendall and Padget,[11] who employed the JKR theory.[12] This theory extended the previous theory by also taking into account the interfacial energy released when two touching spheres deform, thereby reducing their total amount of surface. This is in a way equivalent to introducing Van der Waals forces to interfaces between flexible bodies. Kendall and Padget applied the JKR theory to the situation of dry contacting spheres; i.e., they neglected the force induced by the receding air/water interface. Their result for successful deformation, i.e., when pores completely will have disappeared, depends on the nature of the packing of the particles. For a triangular arrangement, they arrived at

$$G = 9\pi(1-\nu)\frac{\gamma}{r_p}$$

where γ stands for a measure of the surface energy of the polymer, which can, according to Israelachvili[13] be identified with $2\gamma_{pa}$. The parameter ν represents the Poisson ratio, usually being slightly smaller than ½. For other arrangements of the particles,the numerical factor in the formula given goes down, leading to stricter requirements for G.

The JKR theory can also be applied to particles in the presence of either of two types of water/air interfaces. The first one is of the already discussed receding interface in *Figure* 3. The second one is created when, after the receding interface has crossed the whole coating layer, some water may be left as liquid bridges at the contacts between the individual particles, as depicted in *Figure* 5. The attractive forces induced by these bridges are of the same order of magnitude but still smaller than those involved in a receding interface. The liquid bridge force has been analyzed extensively by Schubert.[14] The amount of water left in the bridges during drying is entirely determined by the environmental humidity. As indicted in *Figure* 6, the force is mainly determined by the particle radius ($F \sim r_p^{-1}$) and by the contact angle for wetting.[3]

Surprisingly, the attractive force is virtually independent of the relative humidity (RH), except from RHs very close to unity. It can be argued that this will also hold for the force induced by the receding water/air interface. An important consequence is that no fundamental objection does exist against applying waterborne paints in very humid conditions. Even more, this could lead to better paint performance due to a prolonged open time. Also, the viscoelastic nature of the latex particles would allow more deformation than in a very quick drying process. Evidently, the drying process will proceed much slower, which would require, e.g., other, less volatile cosolvents.

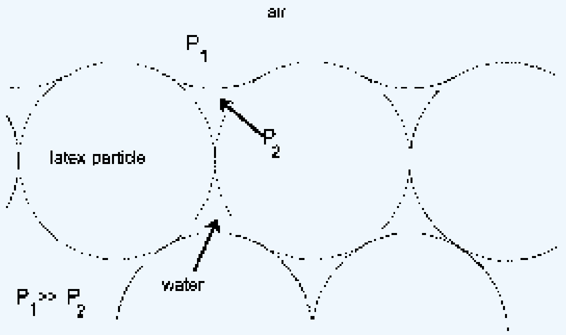

Figure 3—Pressure difference across the surface of a layer of drying latex.

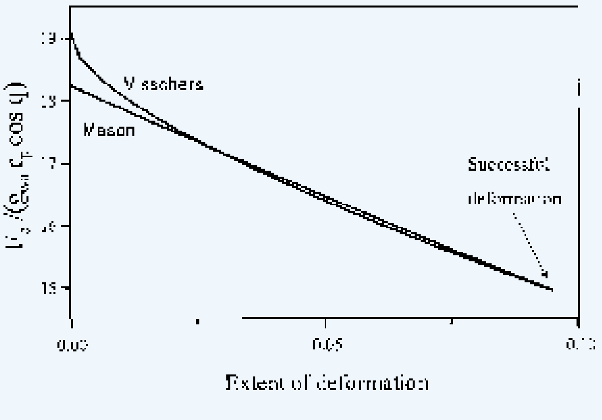

Figure 4—Capillary force due to a receding water/air interface F_C according to Mason and to Visschers et al.

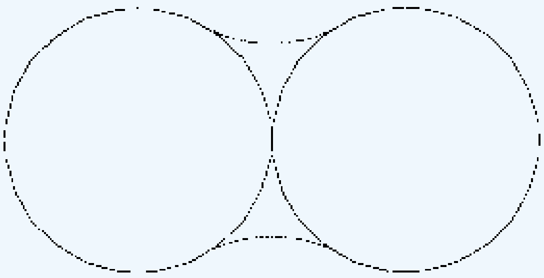

Figure 5—Liquid bridge between two particles.

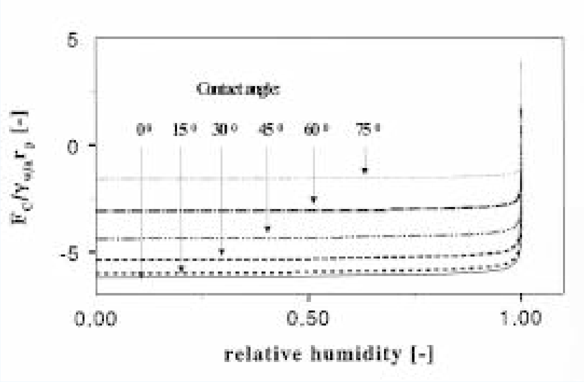

Figure 6—Force due to a liquid bridge as a function of the RH, for various contact angles (r_p=1μm; $\gamma_{w/a}$=0.070 N/m; T=298 K).

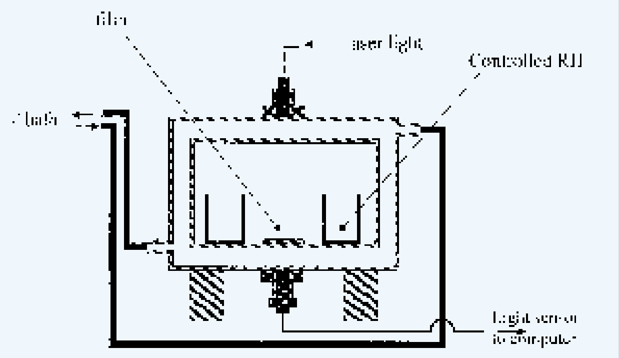

Figure 7—Film drying chamber and the optical detection system.

The conclusion is that all modern theories stress the importance of the (visco) elastic properties of the binder medium. Usually, theories are restricted to elastic properties. A challenge is to investigate the role of the time-dependent rheological behavior. However, this is not an easy job if one aims at measuring this in real paint films.

Regarding the driving forces, all theories agree on the type of driving force: it is surface or interface tension. Stating that it involves Van der Waals forces is not different, as the Van der Waals force is the molecular description of what macroscopically manifests itself as an interfacial tension. However, which interfaces are the most important is not easy to resolve either: all interfacial tensions involved differ by less than one order of magnitude. These conclusions hold also for more realistic waterborne paint systems that also contain, e.g., pigments. Also here it is the binder that has to be deformed in order to avoid air inclusions. As the modulus at the T_g changes so steeply, this property deserves to be studied more carefully for coatings.

EXPERIMENTAL

A film-drying chamber was constructed in which a latex dispersion can be dried at well-defined conditions. The design is depicted in *Figure* 7. A sample of a diluted latex is applied on a microscope slide and inserted in a double-walled glass chamber. Temperature-controlled water is circulated through the wall. With the aid of saturated electrolyte solutions, the RH in the chamber is controlled. The RH of a saturated KCl solution varies from 85.1% at 20°C to 83.6% at 30°C; we will indicate this as RH=84%. For $MgNO_3$, the RH is 53% virtually independent of temperature. Additionally, silica gel was employed to create dry conditions (RH=0%). In order to ensure a homogeneous humidity throughout the chamber, a mini-ventilator (not indicated) induces a slight amount of air convection. The progress of drying is monitored optically as the transmission of the beam of a low-energy laser (633 nm) through the film.

Monodisperse latexes of poly-butylmethacrylate were produced by emulsion polymerization, without the employment of surfactants, using sodiumpersulphate as initiator. The particle size is 250 nm. The zeta potential is –60 mV. The density of the polymer is 1100 kg/m^3. In each test, 600 µl of a 4% v/v latex dispersion was applied on a horizontally oriented glass plate in which a depressed area was created in order to achieve a reproducible surface area of the film. After drying, a polymer film with a thickness of ~32 µm was formed (based on pure polymer without voids). The uncertainty in the quoted final thickness originates from the fact that the drying of the film is not perfectly uniform over the whole film surface, leading to local, slight variations in film thickness.

RESULTS AND DISCUSSION

Influence of the Relative Humidity on Normal Film Formation

In *Figures* 8 and 9, traces of the light transmission through drying films are shown for a range of drying temperatures at RH=53 and 84%, respectively. These conditions represent normal and humid drying conditions. Within a range

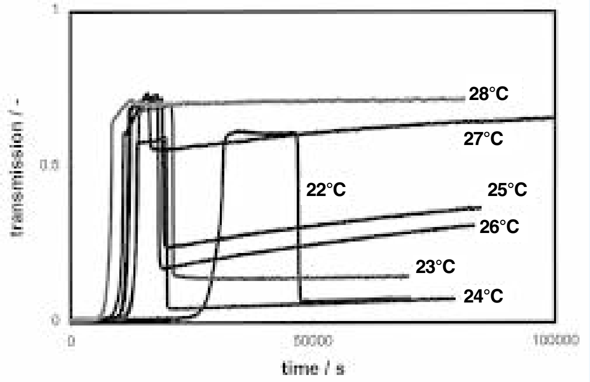

Figure 8—Light transmission during film drying at RH=53%, for various temperatures.

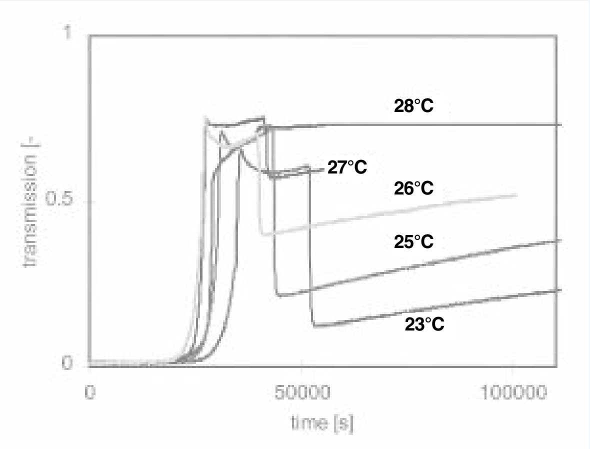

Figure 9—Light transmission during film drying at RH=84%, for various temperatures.

of 5°C, the whole change from successful film formation to virtually no film formation occurs. Usually, after an interval varying with temperature, the latex becomes almost transparent. The explanation for this steep increase in transmission is to be sought in the structure factor for Mie light scattering. The number of scatterers in the film remains the same, but they change their mutual arrangement: they come closer to each other. This is reflected in the scattering factor.

In a few experiments, the temperature within the film was measured simultaneously with the light transmission during drying. Due to water evaporation, the film will be at a temperature slightly below the set temperature due to a noninfinitely fast heat exchange between film and thermostatic wall. Until the maximum plateau was reached, the film temperature appeared to be at a constant level of a few Centigrades below the set isothermal condition. Almost coinciding with attaining the maximum plateau in light transmission, the temperature jumps to a level very close to the set temperature. This indicates that at this point the evaporation rate is reduced drastically. We attribute this to the fact that the air/water interface starts to recede from the surface of the film. The particles are now pushed together by capillary forces. If their (visco) elastic modulus is sufficiently low, they can glue together and coalesce before the water air interface has receded appreciably (at 28°C). This means that in successful film formation the water/air interface remains at the top layer of the particles until the film has coalesced. It can not be ruled out that the reduction in evaporation is partly due to deformation of the particles in the top layer leading to an more or less impermeable top layer. However, this evaporation reduction was also noticed when operating at a lower temperature (see *Figure* 10).

If the temperature is too low, the particles can not coalesce sufficiently quickly. Now, when the air water interface recedes, the interstices are filled with air. Because of the larger difference in refractive indices between particles and the medium in the voids, the film becomes more turbid again. We interpret this as incomplete film formation. It is interesting to note that later on such a film yet may show some progress in film formation. This must be coalescence due to the liquid-bridge mechanism.

Usually the fastest drying occurs near the borders of the film. When the latex particles near the borders start to become stacked, a reduction in the local water pressure within the film is created. This may induce lateral migration of water through the film. This phenomenon is known, e.g., from studies after the rheological behavior of dilatant suspensions,[15] and has also been observed in drying films. We think that this is the reason why the time scales of the transmission traces, although showing a definite overall correlation with temperature, show some scatter. Additionally, it was rather difficult to dose the latex accurately. Especially the 22°C trace in *Figure* 8 shows an unexpected large shift as compared to the other traces. A similar behavior was also noticed in experiments at a low relative humidity (see the following).

At a low RH, a similar set of experiments at a range of temperatures was performed. The results are shown in *Figure* 11. It is clear that the drying is much faster at low RH. As a comparison, at 25°C the peak in transmission is reached after ~3000 s at 0% RH, after 12000 s at 53% RH and after

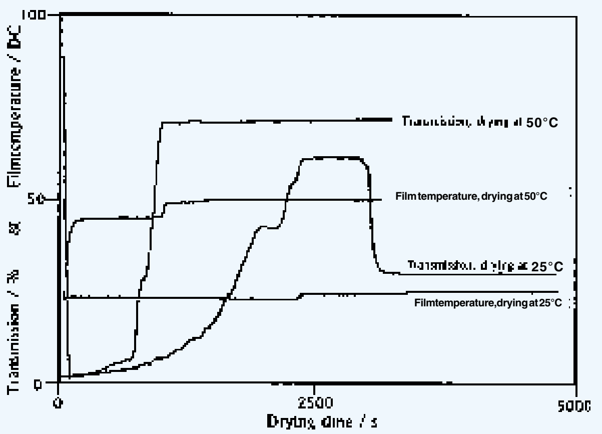

Figure 10—Light transmission and film temperature during drying at RH=0% at different temperatures.

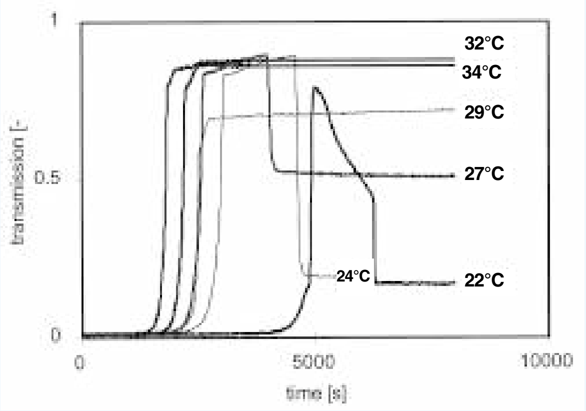

Figure 11—Light transmission during film drying at RH=0%, for various temperatures.

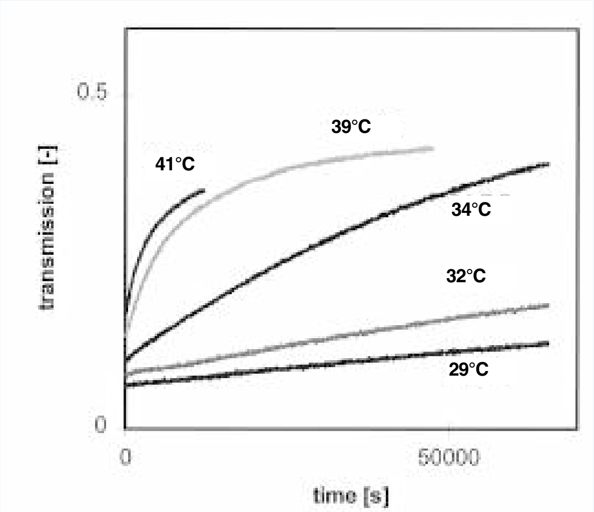

Figure 12—Film formation at various temperatures for latex that was previously dried at low temperature.

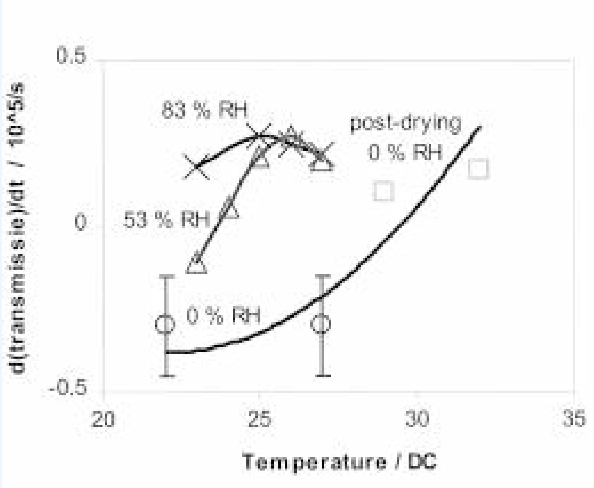

Figure 13—Rate of post-initial film formation for various conditions.

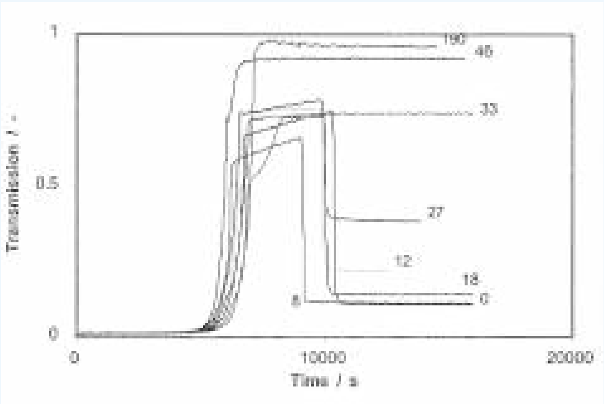

Figure 14—Effect of cosolvent addition (Texanol) on the transmission traces of film drying at 24°C, at 0% RH. The levels are indicated, as mg Texanol / g binder.

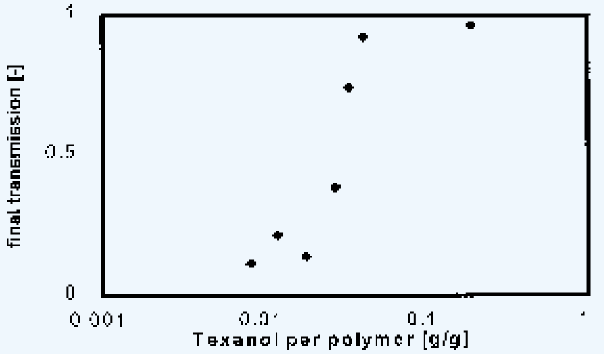

Figure 15—Final transmission values from traces of film formation of Texanol-containing latexes.

30000 s at 83% RH. The critical temperature for successful film formation is not significantly different from the one at normal or at humid conditions. The difference is by no means more than 2°C. However, in the film formed at low humidity, the gradual progress of film formation at a later stage, in previously nonsuccessfully formed films, appears to be absent, or is even negative, within experimental accuracy. This suggests that liquid bridges are now absent. Additionally, water may act as a solvent for the binder, thus weakening the polymer matrix, thereby reducing the modulus, also below the MFFT.

Post-Drying Film Formation and Comparison with Post-Initial Film Formation

A number of experiments were conducted in which the latex was dried at a temperature well below the MFFT. After "completely" drying at 0% RH, they were placed in the conditioned chamber at 0% RH at various temperatures. The results are shown in *Figure* 12. All these systems exhibit post-drying film formation. In order to compare the rates of film formation under the different conditions, the increases in transmission were analyzed for films that had not attained completed (=successful) film formation. This is not an absolute measure for the film formation rate, because when transmission is already large, one would expect that the transmission versus time would level off anyhow. Nevertheless, it seems justified as a relative measure. The results are plotted in *Figure* 13. They indicate a definite influence of the RH on the post-initial film formation rate. The data suggest that the two series of experiments at 0% RH could cover each other. In other words, the "pretreatment" is not critical. A curious phenomenon is that in some cases the transmission gradually goes down with time. Two possible explanations can be given:

(1) The particles do not noticeably deform any more. Any water left in the interstices may evaporate, thereby increasing the amount of voids and the amount of light scattering.

(2) The particles had previously been forced together by the capillary force induced by the receding water air interface. The force left is due to the water bridges between the particles. As discussed in the theoretical section, the latter force is smaller. It may be that the particles exhibit a (visco) elastic recovery thereby generating more void volume and scattering.

It is not possible at this stage to rule out any of these explanations.

Influence of the Cosolvent on Film Formation

As an example of the applicability of the measurement technique, the effect of the addition of Texanol was investigated. As shown before, at 24°C the film formation would be rather incomplete under normal conditions. Therefore, a test series with variable Texanol level was conducted at a film drying temperature of 24°C; the results are plotted in *Figure* 14.

Analyzing the final transmission levels offers a tool for assessing the level of Texanol required for good film formation. These data are shown in *Figure* 15. Note, however, that this is not directly applicable in practice because the latex applied was more dilute than in practice. This has consequences for the drying times, which become larger depending on the volatility of the cosolvent; part of it may have been evaporated when the coagulation starts. However, the testing procedure can be optimized to avoid this problem to a large extent.

The technique presented can also be applied in the evaluation of, e.g., added thickeners and surfactants/ dispersants. It is known that specific combinations of such species can cause phase separation in a latex. The most risky condition usually is with large concentrations, i.e., directly after paint application when water starts to evaporate. However, if one would study this phenomenon under equilibrium conditions this would lead in a too strict stability requirement. It could be that under equilibrium conditions, phase separation occurs, but that the separation proceeds sufficiently slowly so that in the practice of waterborne paint application, phase separation does not occur. This aspect of time is well-known in colloid chemistry: passing from a stable mixture towards the demixing condition, a system first passes the binodal and later also the spinodal (note that binodal and spinodal are lines in a phase diagram that are related to the free enthalpy of mixing). Beyond the spinodal, demixing is instantaneous; before the spinodal, it proceeds much slower. Our technique offers a tool for real-time monitoring of the structure factor of light scattering, which is a direct measure of the degree of demixing.

CONCLUSIONS

Latex-based paints form a continuous film on drying due to the forces induced by the surface tension of the water phase. Depending on the circumstances, the film formation goes along the "easy" route, i.e., by evaporation of "bulk" water, or along the "hard" route, i.e., by evaporation of water from the bridges between the particles. Nevertheless, the surface energy of the polymer air interface, as considered in the JKR model, may play a role under specific circumstances. Successful film formation proceeds along the easy route.

The testing technique presented offers a tool to investigate the progress of film formation. Along with the receding air water interface, the coalescence of the particles should be realized. If the particles have a too large (visco) elastic parameter, they are not able to deform sufficiently quickly, in accordance with the imposed forces. In that case they still will, later on, show some progress in completion of film formation. However, this is on a very much larger time scale than that for successful film formation. The influence of the humidity on the film formation is mainly through the speed of drying of the film, its influence along the route of lowering the modulus or T_g is limited. The testing equipment also allows investigating the effects of additives. In principle, it can also be used with thin layers of pigmented compositions. The equipment especially has potential for dynamic processes, like coagulation during drying, and also for investigating the role of specific additives.

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