

## Formation de couches issues de particules d'eau

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**FORMATION DE COUCHES ISSUES DE PARTICULES D'EAU:  
MECANISME SURFACE-TENSION, EXPERIENCES ET  
DEFAUTS DES COUCHES.**

**J. LAVEN, M. VISSCHERS ET R. VAN DER LINDE**

**Eindhoven University of Technology  
Dutch Polymer Institute, Eindhoven Polymer Laboratories  
PO box 513, NL 5600 MB Eindhoven, The Netherlands  
laven@chem.tue.nl**

**Résumé:**

Les peintures à base de Latex forment une couche continue en séchant, ceci est dû aux forces causées par les tensions à la surface de l'eau. En fonction des circonstances, le film suit le chemin le plus "simple", avec l'évaporation de l'eau, ou par un chemin plus "complexe", avec l'évaporation de l'eau située entre les particules. En suivant le chemin le plus simple, les forces dominantes diminuent lors du procédé de formation des couches. Ce qui explique souvent la non-complète finition des couches.

Une vue d'ensemble est donnée des forces nécessaires à la formation des couches. Il semble alors que la force dominante est l'une des deux forces capillaires. Des complications peuvent intervenir lors de la déformation de deux sphères se heurtant, les sphères perdent alors une partie de leur surface et ainsi réduisent la surface énergétique correspondante; cet effet affecte considérablement la formation des couches. Les forces résistantes considérées par divers auteurs sont élastiques, visqueuses ou visco-élastiques. Dans la plupart des modèles le module de jonction est le paramètre décisif. Ce paramètre a souvent varié, ces dernières décennies, autour de la température de transition du verre  $T_g$ , ce qui explique pourquoi la température de la couche minimale se situe aux alentours de  $T_g$ . Il a été démontré que l'humidité environnante ne joue aucun rôle dans le mécanisme de formation. Le seul effet reste en fait la retardation du séchage (voir la partie expérimentale).

Un système de test expérimental est présenté dans lequel la formation de la couche de dispersion du latex est analysée optiquement. La température et l'humidité sont bien contrôlées. Les résultats montrent les moments des particules se positionnant de façon telle qu'une plus grande transparence est obtenue. De plus, à ce moment un changement dans le refroidissement de l'évaporation suggère un changement dans la vitesse d'évaporation. Certaines particularités dans les données de mesure peuvent

indiquer une migration latérale de la phase liquide. En fonction de la température la couche reste transparente, mais à faible température redevient opaque indiquant le renfermement des vides, la formation incomplète des couches. Les expériences ont montré que l'humidité environnante facilite la restructuration des couches incomplètes. De plus, les effets des additifs , tels les co-solvants, sur les procédés de séchage sont indiqués.

**FILM FORMATION OF WATER BORNE COATINGS:  
SURFACE TENSION DRIVEN MECHANISMS, EXPERIMENTS AND FILM  
DEFECTS.**

**J. LAVEN, M. VISSCHERS AND R. VAN DER LINDE**

**Eindhoven University of Technology**  
~~Dutch Polymer Institute~~, Eindhoven Polymer Laboratories  
PO box 513, NL 5600 MB Eindhoven, The Netherlands  
laven@chem.tue.nl

**Summary:**

Latex based paints form a continuous film while 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. Along the easy route, the driving force reduces as the film formation proceeds. This explains why coatings may have completed only partially.

An overview is given of the forces involved in film formation. It appears that the driving force is either of two different capillary forces. A complicating factor is that when two touching spheres deform, the spheres lose some surface thereby reducing the corresponding surface energy; this has appreciable effect on the film formation. The resistive force considered by various authors is elastic, viscous or visco-elastic. In most models the modulus of the binder is the crucial parameter. This parameter changes over a number of decades near the glass transition temperature  $T_g$ , which explains why the minimum film formation temperature is usually close to  $T_g$ . It is shown that the environmental humidity plays no role in the film formation mechanism per se. The only effect actually is the retardation in drying (see also the experimental part).

An experimental testing device is presented in which the film formation of latex dispersions can be investigated optically. The temperature and humidity are well controlled.

Results show the moment that the particles become stacked in an arrangement with a much larger transparency. Additionally, at that instant a change in evaporation cooling suggests a change in evaporation rate. Some peculiarities in the measurement data might indicate to lateral migration of the liquid phase.

Depending on the temperature the films remain transparent but, at lower temperature, become opaque again, indicating the entrapment of voids, i.e. non-successful film formation.

It was found that the environmental humidity has some effect in "healing" later on of partially formed films. Also, the effect of additives like co-solvents on the drying process will be indicated.

# FILM FORMATION OF WATER BORNE COATINGS: SURFACE TENSION DRIVEN MECHANISMS, EXPERIMENTS AND FILM DEFECTS.

J. LAVEN, M. VISSCHERS AND R. VAN DER LINDE

Eindhoven University of Technology  
Dutch Polymer Institute, Eindhoven Polymer Laboratories  
PO box 513, NL 5600 MB Eindhoven, The Netherlands  
laven@chem.tue.nl

## 1 Introduction

Nowadays, a trend is apparent to replace conventional solvent-based coatings with waterborne ones. In general, those waterborne coatings consist of pigment (e.g.  $\text{TiO}_2$ ), 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 may be successful. A considerable number of authors have dealt with describing this process theoretically. These studies have been reviewed by Vischers et al. [1].

In this paper we will first discuss which of the forces operative in film formation are the dominant ones. The prevailing forces will be evaluated in more detail. We will 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.) will be discussed. Then, an experimental film-drying cell will be presented and the results obtained will be presented. Other potential application to investigate the performance of waterborne paints will be discussed as well.

## 2 Theory of Film Formation

### 2.1 *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 non-transparent, powdery film. This opacity indicates that there are still many residual voids left within the film, 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 is evidently driven by a reduction of the interfacial energy; it is called coalescence. It is depicted in Figure 1.

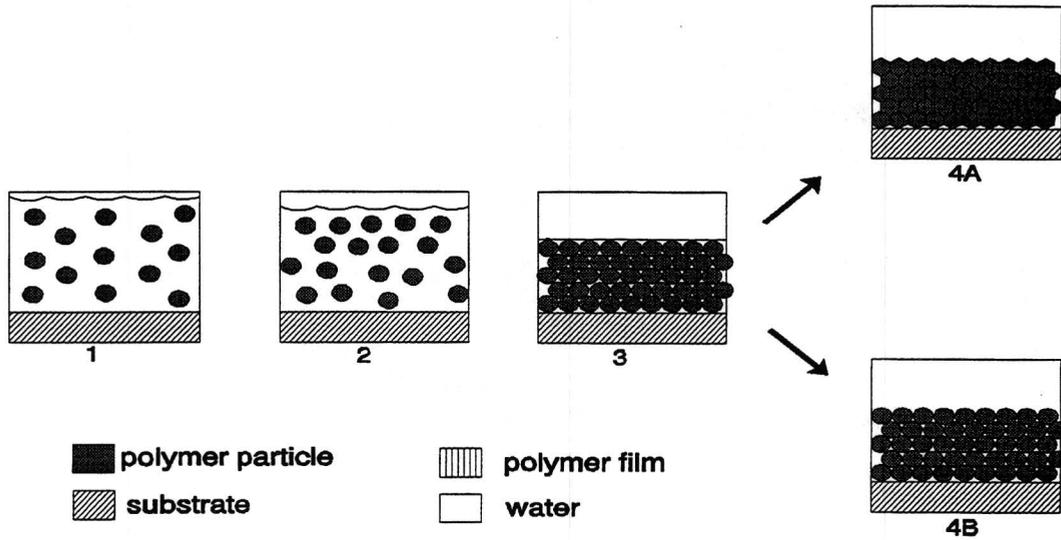


Figure 1: Drying of latex film beyond (route A) and below  $T_g$  (route B).

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 forces operative are depicted in Figure 2. Of these forces, only the Coulomb' and the deformation forces are usually 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 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 Section. Note that capillary forces are only effective in film formation when the binder is a surface for which water is a wetting agent (contact angle  $\theta < 90^\circ$ ). In a separate paper we demonstrated that this is the case, even for the relatively hydrophobic polystyrene latex in the absence of surfactants [2].

type of force	estimated force / N
gravitational	$6.4 \cdot 10^{-17}$
Van der Waals (hard spheres)	$5.5 \cdot 10^{-12}$
electrostatic	$2.8 \cdot 10^{-10}$
capillary (receding W/A interface)	$2.6 \cdot 10^{-7}$
capillary (liquid bridges)	$1.1 \cdot 10^{-7}$
elastic deformation	$1.0 \cdot 10^{-7}$

Table 1: Typical values for forces operative during drying of binder films. particle radius  $r_p$ : 250 nm; Hamaker constant:  $1.05 \cdot 10^{-20}$  J; electrical surface potential: -20 mV; salt level: 1mM; surface tension of water: 70 mN/m; contact angle:  $0^\circ$ ; polymer modulus:  $10^7$  N/m<sup>2</sup>.

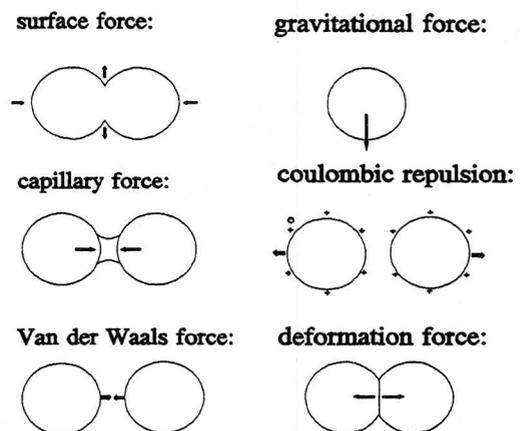


Figure 2: Forces operative in binder film formation.

## 2.2 The 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 ( $\gamma_{pa}$ ). 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).

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 does. 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 ( $\gamma_{wa}$ ) was responsible for particle deformation. 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 even below  $T_g$ , after the removal of water, some progress in film formation is possible. This indicates that  $\gamma_{pa}$  may still play a role.

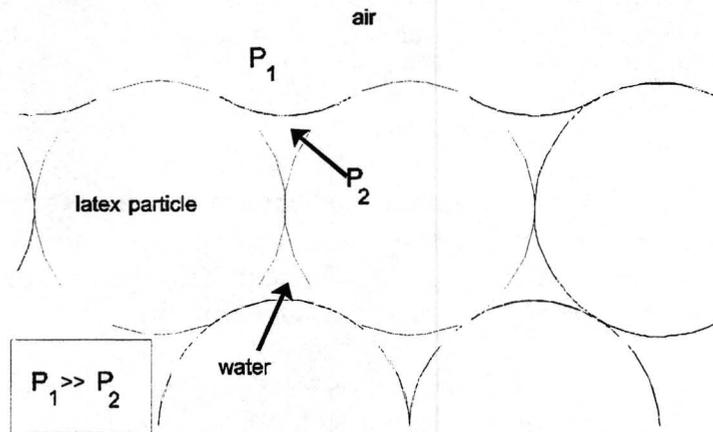
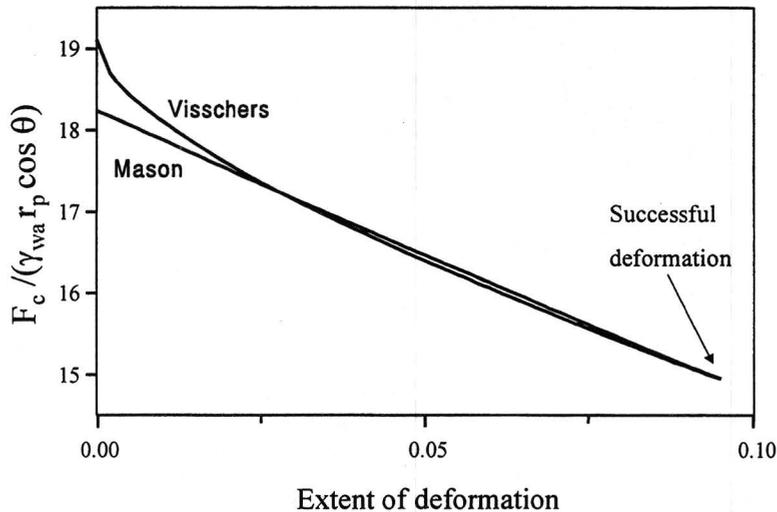


Figure 3: The pressure difference across the surface of a layer of drying latex.

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' 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. 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 tensions [3]). In this graph, successful deformation leading to a homogeneous film is realized at an "extent of deformation" of 0.95.



**Figure 4:** The capillary force due to a receding water/air interface  $F_c$  according to Mason and to Visschers.

As with progressive deformation the contact area between the particles increases, the resultant stress induced in the particle ( $\sim$ force/area) drops down even more. Thus, not all films that start to deform by capillary forces, will actually 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, up till 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 visco-elastic one. He also corrected a flaw in a pre-factor as produced by Brown and Mason. His approach, which implicitly contains a rate dependent resistance, would also allow assessing the speed of film formation. A point that has not been resolved up till now is that the deformation of the particles is too large to assume linearity of the visco-elastic material properties.

A completely different approach was followed by Kendall and Padget [11], who employed the JKR theory [12]. This theory extends 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  $\gamma$  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  $\nu$  represents the Poisson ratio, usually being slightly smaller than  $\frac{1}{2}$ . For other arrangements of the particles the numerical factor in the formula given goes down, leading to stricter requirements for  $G$ .

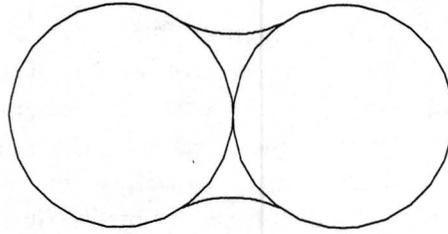


Figure 5: Liquid bridge between 2 particles

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 indicated 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, it appears that with latexes the attractive force is virtually independent of the relative humidity (RH), except from RH's very close to unity. It can be argued that this also will 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 prolonged open time. Also, the visco-elastic 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, co-solvents.

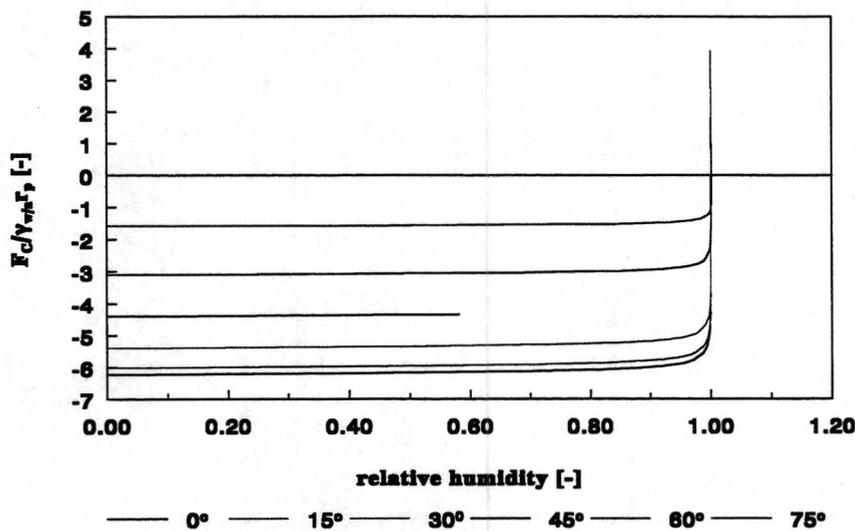


Figure 6: The force due to a liquid bridge as a function of the relative humidity, for various contact angles ( $r_p=1\mu\text{m}$ ;  $\gamma_{w/a}=0.070\text{ N/m}$ ;  $T=298\text{ K}$ ).

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.

About the driving forces: all theories agree on the type of driving force: it is surface or interface tension. Saying that it are 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 e.g. contain pigment. Also here it is the binder that has to be deformed in order to avoid air inclusions. As the modulus at the glass temperature changes so steeply, this property deserves to be studied more carefully for coatings.

### 3 Film drying experiments and discussion

#### 3.1 Experimental

A film-drying chamber was constructed in which latex dispersion could be dried at well-defined conditions. The design is depicted in Figure 7. A sample of 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 relative humidity 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<sub>3</sub> 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.

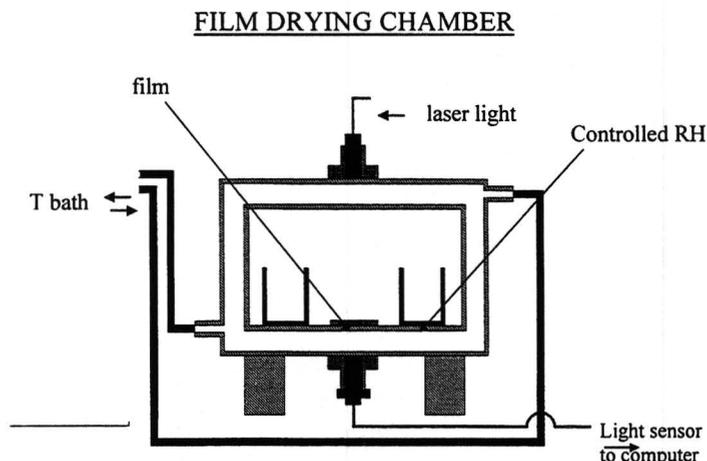
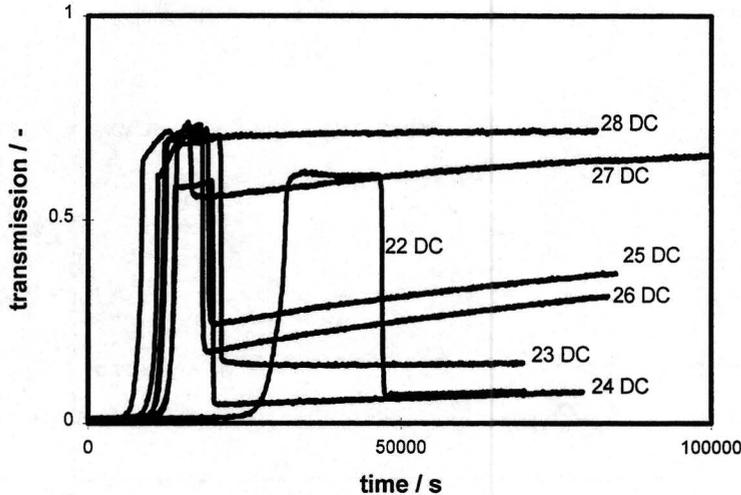


Figure 7: The film drying chamber and the optical detection system

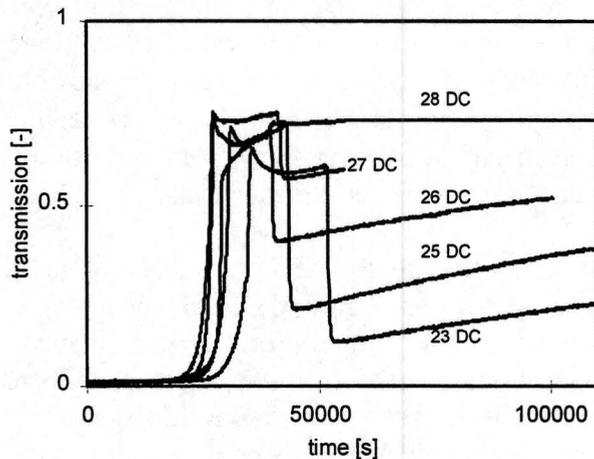


**Figure 8:** Light transmission during film drying at RH=53 %, for various temperatures

Monodisperse latexes of poly-butylmethacrylate were produced by emulsion polymerization, without 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  $1100 \text{ kg/m}^3$ . In each series of tests the same amount of suspension and of volume fraction of binder particles was used. However, between the series some differences exist in this respect.

### 3.2 *The influence of the relative humidity on normal film formation.*

In Figure 8 and Figure 9 traces of 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 of 5 degrees Centigrade 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 step 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.



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

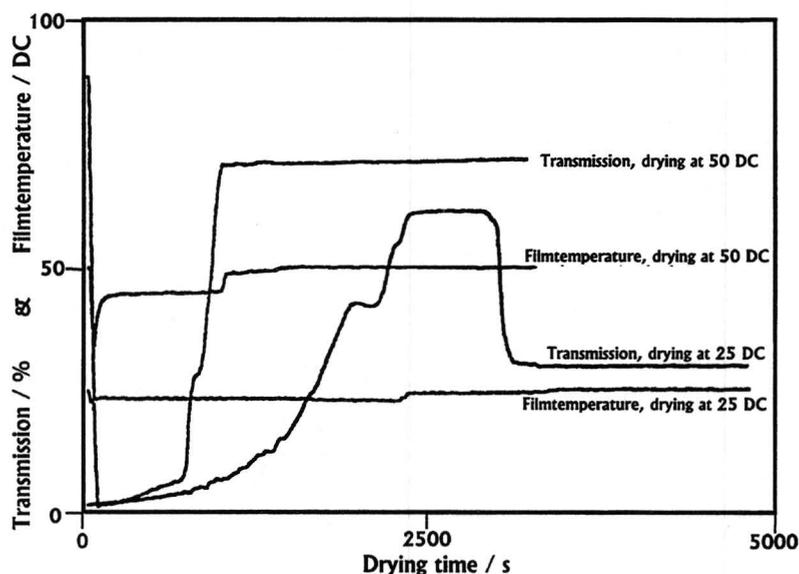
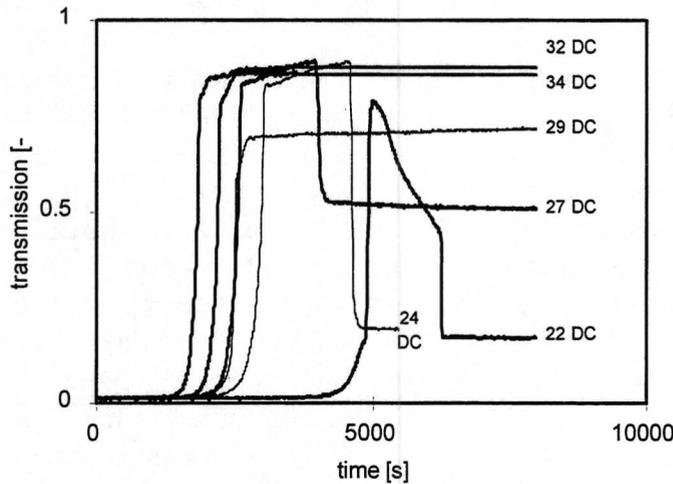


Figure 10: Light transmission and film temperature during drying at RH=0 % at different temperatures.

In a few experiments simultaneously with the light transmission also the temperature within the film was measured during drying. Due to water evaporation the film will be at a temperature slightly below the set temperature due to a finite heat transfer coefficient. 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 that has therefore become less permeable due to coalescence. 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. When now 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 shows some progress in film formation. This must be coalescence due to the liquid-bridge mechanism.

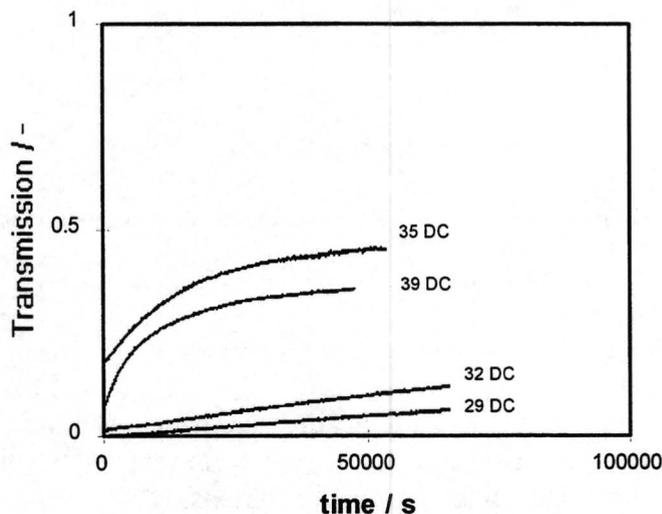
Usually the fastest drying occurs near the borders of the film. When the latex particles near the border start to be stacked, a reduction in the local water pressure within the film is created. This may induce lateral migration of water through the film. This phenomenon is known e.g. from studies after the rheological behavior of dilatant suspensions [15], and has also been observed in drying films. We think that this is the reason that the transmission traces, although showing a definite overall correlation with temperature, show some scatter. Additionally it was rather difficult to dose the latex



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

accurately. Especially the 22 °C trace 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 below).

At a low relative humidity 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 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 degrees Centigrade. However, in the film formed at low humidity, the gradual progress of film formation in non-successfully formed films at a later stage appears to be absent, 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.



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

### 3.2 *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 was analysed for films that had not attained successful film formation. This is not an absolute measure for 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:

- (i) the particles do not noticeably deform any more. Any left water in the interstices may evaporate, thereby increasing the amount of voids and the amount of light scattering
- (ii) The particles had previously been forced together by the capillary force induced by the receding water air interface. The force left is that 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 an elastic recovery thereby creating more void volume and scattering.

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

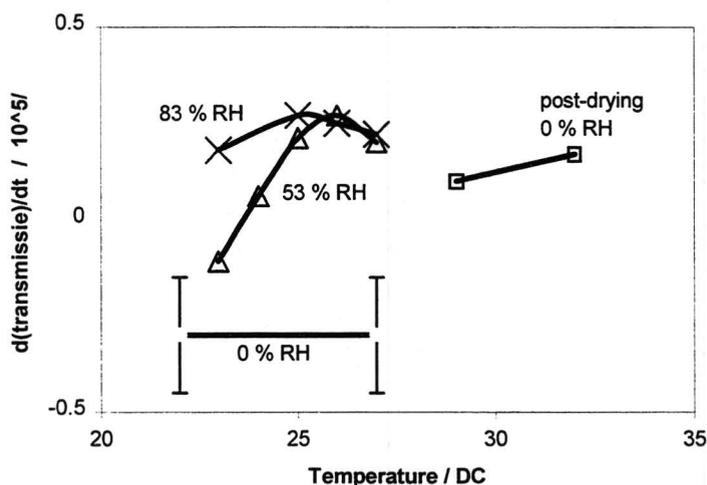
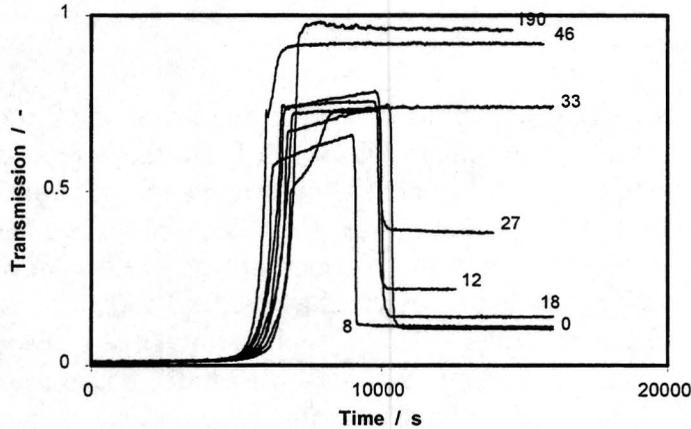


Figure 13: Rate of post-initial film formation for various conditions

### 3.3 *The influence of the co-solvent on film formation.*

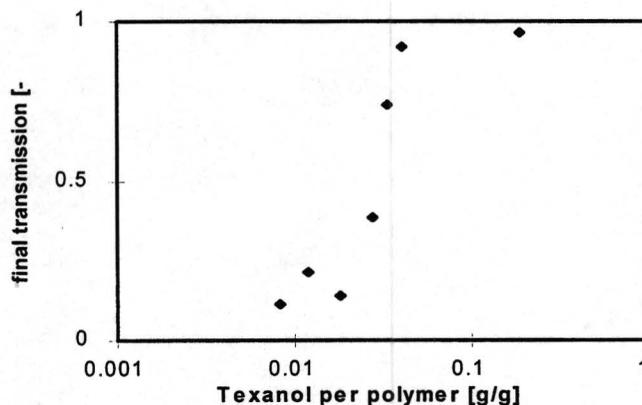
As an example of the applicability of the measurement technique the effect of the addition of Texanol was investigated. As shown before, at 24 °C the film formation would be rather incomplete under normal conditions. Therefore, a test series with variable Texanol level was conducted at a film drying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



**Figure 14:** The effect of co-solvent addition (Texanol) on the transmission traces of film-drying at 24 °C, at 0 % RH. The levels are indicated, as mg Texanol / g binder.

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 co-solvent, 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. 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 at 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 slow so that in the practice of waterborne paint application it 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.



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

#### 4. 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.

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 accord with the imposed forces. In that case they will later on yet show some progress in completion of film formation. However, this is on a very much larger time scale than that of 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. However, it can not be used with 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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D) DeMartean UCB: samen met Winnik; gelijke  $T_g$  maar  
(Tielmans) variabele crosslinking → grote verschillen in MFT

Leo VanderVen Er is reeds veel aan gedaan.  
Hij zal diss. uit UT opzoeken over transmissie