❊ *Third Place Winner in 1995 Roon Awards Competition* ❊

Coalescence and Film Formation from Latexes

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A paint is a complex liquid coating material composed of pigments, fillers, polymeric binders, and other additives dispersed and/or dissolved in a liquid. When applied to a surface, the liquid is changed by a film forming process to a solid, adherent composite film. The formation of a paint film is so spontaneous and familiar that most give little thought to the mechanism and dynamics of the process. Yet it is the dynamics of film formation that can provide perspective to the design and application of polymeric latexes.

Previously, a number of workers have studied the "mechanism" by which the latex particles coalesce with each other.[1-5] Their attention has been focused on the details of how particle-particle contacts and interactions take place. It is the author's intent to emphasize the thermodynamics of the filming process. A general theory of film formation from a paint is derived from thermodynamic considerations. Model calculations are made and the results are encouraging. They are able to predict the effect of pigmentation and identify new areas for polymer and formulation research. The theory is capable of being specialized for either solvent or latex systems.

FILM FORMATION SOLVENT-BORNE PAINT

A properly formulated solvent-borne paint is one in which the pigments and fillers are prewet by the solvated vehicle. In effect the pigment and filler particles have adsorbed a highly solvated layer of polymer (entropic stabilization) on their surface. The adsorbed layer is composed of the higher molecular weight fraction of the solvated polymer vehicle.

Upon application, the solvents begin to evaporate and the film begins to shrink. Since length and width of the film are nearly constant, the volume loss is primarily in thickness of the film. The rate of solvent loss on drying mirrors the change in thickness that takes place. At first, the solvent loss is rapid and mainly a function of evaporation potential (vapor pressure) of the solvent. The next stage of film formation is the loss of solvent transitions from a solvent vapor pressure driven process to a slower diffusional process of solvent through the ever increasingly viscous polymer matrix.

If the pigmentation, i.e. pigment volume concentration (PVC) of the paint is well below a critical level, termed critical pigment volume concentration (CPVC), then continued solvent loss concentrates the binder until the increase in viscosity/modulus of the binder immobilizes the film. Further loss of volume creates stress throughout the film.[6-9] At PVCs near or at the CPVC, the shrinkage continues until there is an overlap of the entropic layers adsorbed on the pigment particles, at this point the anisotropic shrinkage causes the development of local strains. These strains continue to increase with loss of solvent and reach a maximum when the pigment particles come in contact with each other or the modulus of a localized region of the vehicle has increased to the point which prevents further relaxation of these localized strains. Thus, in any dry paint film, two types of residual strain can be identified: (1) transverse strains,[†] i.e., strains distributed over the length and width of the film; and (2) localized strains, strains that are between neighboring domains or particles of pigments and fillers.

Even though much of the stress is relieved with time, there are always residual strains which are frozen into the paint film. These residual strains can lead to the destruction of the paint film; the transverse strains are responsible for adhesive losses, i.e., peeling failure and blistering of the paint film while the

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[†] In the work cited in references 6-9, these strains are referred to as internal strains. In this work, the designation of transverse strain is preferred to indicate that they operate across the length and width of the paint film.

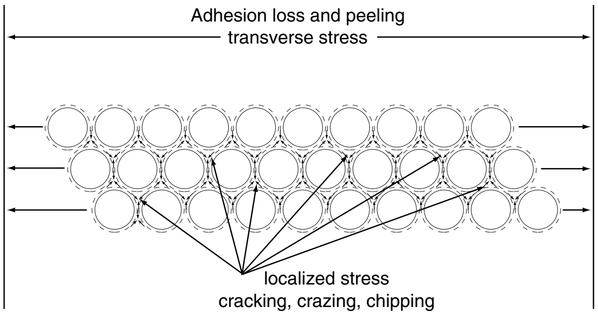

Figure 1—Schematic model illustrating both transverse stresses and local stresses induced by film forming process in an adherent film. Transverse stresses are across the length and width of the film, while the localized stresses are between neighboring regions of the paint.

localized strains cause cracking, cold checking, alligatoring, etc. *Figure* 1 is a schematic model of filming stresses in a paint.

FILM FORMATION FROM LATEX PAINTS

A latex paint consists of highly dispersed pigments and a well-stabilized polymer particle in an aqueous fluid phase. In contrast to a solvent-based paint, the pigment and fillers are not prewet by the polymer vehicle. Each element, pigment, filler, and polymer particle are independently stabilized. In a properly formulated paint, both latex and pigment particles show little tendency to flocculate or agglomerate.

Upon application and formation of a film, the pigments and latex polymer particles must encase the pigment particles and bind them within the glassy polymer matrix. The latex film forming process can be considered to take place in three distinct stages: (1) the concentration stage; (2) the compaction stage; and (3) the gradual coalescence stage.

The Concentration Stage: During the concentration stage, the initial water loss mimics the rate of evaporation of water alone.[10] The loss of water causes crowding or gathering of both the polymer particles and the pigment particles. As the crowding becomes more stressed, the particle stabilization layers on both pigment and polymer particles (both entropic and electrostatic double layer) resist further concentration and initiate a “redistribution” of the particles in the film to maintain the lowest energy state possible. Depending upon the particle sizes of pigment and latex, there is a predisposition for the smaller to concentrate in the free interparticle space of the larger[11,12] until the critical packing of the system is attained.[*]

The Compaction Stage: The onset of critical packing, K_c, marks the beginning of the compaction stage. With further loss of water, failure of the stabilization layers occurs; the more robust persisting the longer, but it too will ultimately collapse and further compaction of the film by evaporative losses causes polymer particles to deform or begin coalescence; neighboring pigment particles form clusters.

The Gradual Coalescence Stage: In the last stages of drying, the continued loss of water requires: (1) that the polymer particles flow together, wet, and surround the pigments; or (2) alternatively if flow is not possible, the polymer and pigment particles dewet at stress concentration points, and a cohesive fracture of the tender semi-solid film (mud cracking) takes place.

Although the film has the appearance of being dry, coalescence continues for some time, and the paint film properties continue to develop for several days. The gradual coalescence process is driven by the creep compliance or relaxation of induced stresses caused by the loss of volume and adherence of the film to the substrate.

Because of constrained packing at the substrate and the air boundaries, the first zones of the film to reach critical packing are the film edges and thin areas, e.g., brush and stipple marks. These film zones have a much higher viscosity and at the same time are the first areas to initiate coalescence. Therefore, film formation moves in a lateral manner emanating from the point or first zones of coalescence.[13]

VOLUME RELATIONSHIPS

Basic Volume Definitions

A coating is expected to have a number of properties, many of which are directly related to the arrangement of the particulate materials (pigments and fillers) in the element of volume (vehicle). Because we are dealing with how particles of matter occupy space, it is more convenient to work with volume relationships rather than mass.

Consider an element of volume, v_e, in which there is dispersed or suspended particulate matter of such size that the volume, v_i, of any individual particle is very small with respect to the volume of the element. The total volume, $\sum v_i$, of the particles is the summation of the volume of the individual particles. The ratio of the volume of particles to the element of volume is defined as the volume concentration, ϕ, in equation (1).

$$\phi = \frac{\sum V_i}{V_e} = \frac{V_{particles}}{V_e} \qquad (1)$$

Let us envision a suspension of a particulate material dispersed in a volume of fluid, and let us increase the number of particles until each particle is in contact with each of its nearest neighbors. Although there is enough fluid to wet and fill the voids space between all the particles, movement of particles is impossible.

Table 1—Coatings Properties as a Function of CPVC

Property	Below CPVC	Above CPVC
Gloss	High	Low
Porosity	Low	High
Dirt pickup	Low	High
Modulus at break	Low	High
Elongation at break	Flexible	Brittle
Water permeability	Low	High

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[*] In this description of film formation, it is assumed the system is below CPVC.

The system is said to have reached critical packing, and the free volume of the system is now zero, i.e., the particles are so crowded into the element of volume that they are not free to move. The ratio of the volume of particles to the total volume, i.e., sum of the volume of particles plus the volume of the fluid when each particle is in contact with its nearest neighbors, is the critical packing constant for the dispersion. The free volume (V_{free}) of the original suspension is given by equation (3). From equation (3) it is apparent that when ϕ is equal to K_c the free volume is zero.

$$K_c = \frac{\sum V_i}{\sum V_i + \text{Void Volume}} = \frac{V_{particles}}{V_{particles} + \text{Void Volume}} \quad (2)$$

$$V_{free} = 1 - \frac{\phi}{K_c} \quad (3)$$

The properties of a coating are directly related to the volume occupied by the particulate material (pigments and fillers) per element of volume of the system (vehicle volume plus particulate volume). This basic concept of pigment volume concentration was introduced to the coatings industry by Asbeck and Van Loo.[14] They were able to identify a unique PVC at which nearly all of the coating properties underwent a dramatic transition, usually from good to poor (see *Table* 1). This unique property was termed the critical pigment volume concentration. Coatings technologists have successfully explained many performance properties of coatings using this simple concept. CPVC is a specific application of a more general relationship.

Both PVC and CPVC are volume relationships in the solid dry film of the paint, while ϕ and K_c refer to the volume relationships in the liquid paint film. These volume relationship definitions are key to the development of a general filming theory for latex paints.

Volume Relationships in Solvent Paints

In a properly formulated solvent-based coating, it is assumed that particles of pigments are uniformly encompassed by an adsorbed layer of the polymer vehicle. In the dry paint film, CPVC can be defined as that unique PVC in which the volume of binder is sufficient to encapsulate and fill the voids between the pigment particles. Most solvent-based paints are formulated well below the CPVC. In solvent paints the polymer vehicle is an integral part of the fluid phase.

$$PVC_{solvent\ paint} = \frac{Volume_{pigments}}{Volume_{pigments} + Volume_{binder}} \quad (4)$$

Volume Relationships in Latex Paints

In latex paints, the concept of CPVC, while remaining generally valid, the relationship must be modified[15] to describe correctly the pigment volume relationships, i.e., the amount of pigment required to attain CPVC is highly dependent not only on the packing characteristics of the pigment, but on the properties of the polymer and the particular latex vehicle as well. The exact manner in which particles of latex polymer and pigment particles interact influences the distribution of pigments and fillers in a paint film and plays an important role in determining the CPVC of the paint, appearance, film coalescence, residual film stress, and performance of the paint composition in general. It is suggested that a more general equation for CPVC would include a constant (b), an adjustable term which is a function of latex particle size, pigment particle size, and the shear modulus of the polymer, which in turn is a function of T_g and molecular weight. In a solvent-borne paint, b is equal to 1. *Figure* 1 is an approximation* of the CPVC of a latex as a function of particle size of both the pigment and latex. A more accurate relationship would necessarily include modulus term. In the calculation, average pigment size is 0.2 microns and the CPVC in a solvent system is 46.0%.

$$CPVC_{latex\ paint} = \frac{V_{pigment}}{V_{pigment} + b \cdot V_{vehicle}} \quad (5)$$

where b = 1, solvent paints
b > 1, latex paints

In contrast to solvent paints, the latex is not a part of the fluid phase, but rather discrete particles suspended along with the pigment and filler particles. As a result we can write a new volume relationship which describes the latex composition:

$$\phi_{Latex\ Composition} = \frac{V_{Polymer} + V_{Pigment} + V_{Filler}}{V_{Polymer} + V_{Pigment} + V_{Filler} + V_{Aq.\ Phase}} \quad (6)$$

In the film forming process, as the water evaporates, the latex composition approaches and eventually exceeds the critical packing, i.e., $\phi_{composition} \geq K_c$ and as a consequence, drying composition must take one of the following paths:

(1) If the latex polymer particles can deform, i.e., they coalesce and flow around the pigment particles, a film is formed; or

(2) If the latex particles cannot deform, the aqueous phase will dewet from the pigments, polymer, and substrate, therefore, cracks form in the composition.

The exact path the drying composition will take depends on polymer modulus as a function of T of the polymer and the packing of the pigment/filler composition.

THERMODYNAMIC CONSIDERATIONS

Although it is possible to develop polymeric materials by emulsion polymerization that can be dried and redispersed, film formation from latex compositions generally is an irreversible process. It occurs only when the forces driving film formation exceed the forces which would maintain the dispersed state. It will be remembered that much work was done on the system to insure stability, i.e., the adsorption of ionic species and surfactants ($Q_{electrostatic}$) to form double layers, the solvation of hydrocolloids by water ($Q_{entropic}$), and their adsorption or grafting to the polymer surface to form entropic layers. These layers create energy barriers to London-Hamker's attractive forces, which much be surmounted if film formation is to occur. But even after the particles are in contact with each other, there is work required to cause the polymer particles to coalesce ($Q_{coalescence}$) into a coherent film. The work of film formation, Q_{ff}, must counteract and exceed the sum of these forces before film formation can take place.

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* $$b \approx \left[\frac{size_{pigment} + \frac{size_{latex}}{2}}{size_{pigment}} \right]^{\frac{1}{3}}$$

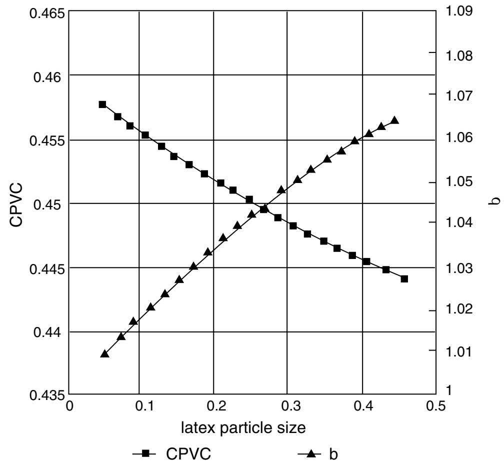

Figure 2—Estimated CPVC of a latex as a function of the particle size and average pigment particle size. Calculation assumes: pigment particle size 0.2 microns, and a pigment packing of 46.0%.

$$Q_{ff} > Q_{electrostic} + Q_{entropic} + Q_{coalescence} \tag{7}$$

Clearly, the one and only force which offsets the stability barriers and facilitates film formation is driven by the evaporation of water.[16,17] The extreme loss of water causes the collapse of double and entropic layers. Further, the loss of water results in a volume shrinkage of the liquid film. It is the liquid film shrinkage, which in combination with the surface forces causes flow and consolidation of the polymer particles to a coherent coalesced film.

The free energy of evaporation is given by:

$$\Delta G_{vap} = \Delta E_{vap} + P\Delta V_{vap} - T\Delta S_{vap} \tag{8}$$

Where ΔE_{vap} is the energy of vaporization of water, $P\Delta V_{vap}$ is the work done by the system to expand the water vapor against the atmosphere. Both of these energy terms represent energy consumed by the evaporation of the water itself, which must be supplied from the surrounding environment. Thus we can write the inequality:

$$T\Delta S_{vap} > \Delta E_{vap} + P\Delta V_{vap} \tag{9}$$

From this reasoning it can be concluded that the filming process is entropy driven and the available energy to do useful work from the surroundings must be greater than the energy required for film formation (Q_{ff}), equations (10) and (10a).

$$Q_{useful\ work} = T\Delta S_{vap} - \Delta E_{vap} - P\Delta V_{vap} \tag{10}$$

$$Q_{useful\ work} > Q_{ff} \tag{10a}$$

The energy required for film formation (Q_{ff}) can be divided into two discrete components. The work required for the concentration stage I, ($Q_{concentration}$), and the work of compaction and coalescence, stage II, ($Q_{coalescence}$), is shown in *Figure* 3 and equation (10b).

$$Q_{ff} = Q_{concentration} + Q_{coalescence} \tag{10b}$$

The work of concentration is the energy required to force particulate matter into close proximity to one another, and is directly related to the change in viscosity, a function of ϕ, times the shear rate as the rapid evaporative stage I process proceeds, see equation (10c). It has been found[18] that the rate of evaporation under "normal conditions" is about 85% of that of pure water.

$$\begin{gathered} Q_{concentration} = Q_{electrostatic} + Q_{entropic} \\ Q_{concentration} = \bar{\gamma} \int_{\phi}^{K_c} \partial \eta_{paint} \end{gathered} \tag{10c}$$

It is, however, the work of coalescence, stage II, that is the main focus of the present paper, for it is at this point the process becomes irreversible. It is stage II that the paint technologist and polymer chemist must address in the design of new latex systems.

Since work can be defined as $P\Delta V$, the work of coalescence must be equal to the complex shear modulus ($M_{film}{}^*$) of the coating (pressure), at the temperature the film is being formed, times the volume change in the film as ϕ changes from K_c to 1 (dry film), equation (11).

$$Q_{film\ coalescence} = M^*_{film}\ \Delta V_{film_{K_c \to 1}} \tag{11}$$

The volume change can be obtained by rearranging equations (1) to (11a), and differentiating with respect to the volume concentration at constant polymer volume, equation (11b). Integrating of equation (11b) between the limits K_c to 1 gives the film volume change during coalescence, equation (11d).

$$V_{film} = \frac{V_{polymer}}{\phi} \tag{11a}$$

$$dV_{film} = -V_{polymer} \frac{d\phi}{\phi^2} \tag{11b}$$

$$\Delta V_{film} = V_{polymer} \int_{\phi - K_c}^{\phi - 1} \frac{d\phi}{\phi^2} \tag{11c}$$

$$\Delta V_{film} = V_{polymer} \left[1 - \frac{1}{K_c} \right] \tag{11d}$$

The volume of the polymer/unit area of the film is estimated from equation (12). If it is assumed that the area of the film is nearly constant and only the thickness of the film changes, $V_{coating}$ can be defined in terms of $t_{dry\ film}$, the dry film thickness, equation (13).

$$V_{polymer} = V_{coating} \left(1 - \frac{PVC}{100} \right) \tag{12}$$

$$V_{coating} = Area_{coating} \cdot t_{dry\ film} \tag{13}$$

In a pigmented system, it is the complex shear modulus of the pigmented system ($M_1{}^*$) rather than the shear modulus of the pure polymer ($M^*_{polymer}$) that is important; the shear modulus of the pigmented film can be related to the shear modulus of the pure polymer times a function (β) that describes the packing and reinforcing character of the pigments, equation (14).

$$Q_{coalescence} = \beta\ M^*_{polymer}\ V_{polymer} \left[1 - \frac{1}{K_c} \right] \tag{14}$$

Some have suggested that theoretical expressions for viscosity and shear modulus should be of the same form.[19] From this reasoning one might imply that a Mooney model [equation (15)] could be used to estimate the reinforcing character of a pigment or filler; however, it is known that a direct transposition of the Mooney expression overstates the reinforcing character of a pigment or filler even when corrections have been made for the binder polymer not being elastomeric (Poisson's ratio < 0.5) and the shape of the particles are not spherical.

$$J = J_o \exp\left[\frac{2.5\ \text{pvc}}{1-\frac{\text{pvc}}{\text{cpvc}}}\right] \tag{15}$$

The Kerner equation is reported to be much more accurate at reasonable filler ratios and could be used as an alternative to the Mooney model; however, the Kerner equation is a continuous function and does not display the discontinuity at CPVC that exists. For these reasons it is reasonable to modify another free volume expression which will display a discontinuity at CPVC. The Doolittle equation may represent such a model, equation (16a). The function ß, then must include four factors: (1) a free volume function of the PVC and CPVC; (2) a function of Poisson's ratio of the binder polymer; (3) a term describing the shape/orientation of the pigments/fillers in the paint film; and (4) the shear modulus of the pure polymer. Recasting the function ß in term of the Doolittle equation yields equation (16b).

$$J = J_o \exp\left[\frac{b}{V_{\text{free}}}\right] \tag{16a}$$

$$\beta = \exp\left[\frac{f_{(\nu 1,\,\Xi)}\ \text{CPVC}}{\text{CPVC}-\text{PVC}}\right] \tag{16b}$$

$$M_1^* = M_{\text{polymer}}^* \exp\left[\frac{f_{(\nu 1,\,\Xi)}\ \text{CPVC}}{\text{CPVC}-\text{PVC}}\right] \tag{16c}$$

The general relationship for the function ($f_{\nu 1,\Xi}$) in the case of shear deformation for any Poisson's ratio is given by equation (17). When spherical particles are dispersed in a liquid, $f_{\nu 1,\Xi}$ reduces to 2.5 (Einstein's coefficient or 2.5). The value of Poisson's ratio for ideal elastomer approaches that of a liquid (0.5); Poisson's ratio for a polymer below its T_g (glassy solid) is approximately 0.35.

Like modulus, Poisson's ratio passes through an inflection as the temperature increases from below the glass temperature, T_g, to above the glass temperature. Thus, a temperature dependent filming model must necessarily relate both polymer modulus and Poisson's ratio as a function of temperature.

$$f_{(\nu 1,\,\Xi)} = \Xi \cdot \left[\frac{15\,(1-\nu_1)}{8-10\nu_1}\right] \tag{17}$$

where:

ν_1 = Poisson's ratio of polymer at filming temperature
Ξ = pigment particle shape factor (spheres = 1)

Substitution of equations (12), (13), and (16b) into equation (14) gives a working model [equation (18)] for the energy required to completely coalesce a latex paint film. Much of the needed data is expressed in terms familiar to the paint technologist.

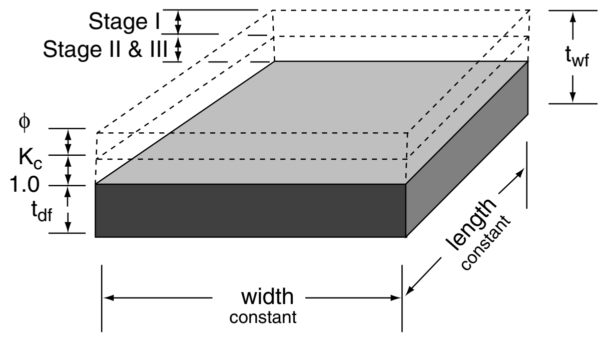

Figure 3—Diagram illustrating volume changes during film formation of a latex composition, Concentration Stage I—$Q_{concentration}$, Compaction Stage II—$Q_{coalescence}$.

$$\frac{Q_{\text{coalescence}}}{\text{Area}_{\text{coating}}} = M_{\text{polymer}}^* \exp\left[\frac{f_{(\nu_1,\Xi)}\ \text{CPVC}}{\text{CPVC}-\text{PVC}}\right]\left[1-\frac{1}{K_c}\right]\left[t_{df}\left(1-\frac{\text{PVC}}{100}\right)\right] \tag{18}$$

The degree or percent coalescence can be defined as:

$$\%\ \text{Coalescence} = \frac{\phi_{df}-K_c}{1-k_c}\times 100 \tag{19}$$

The cohesive forces holding the liquid film together are the surface tension of the water and interfacial tension between water and the wetted particles. These forces are the work of adhesion and the work of cohesion. They are approximately numerically equal to the work of dewetting and liquid film rupture. They are given by:

$$W_{wp} = \gamma_w + \gamma_p - \gamma_{wp} \tag{20}$$

$$W_{w,poly} = \gamma_w + \gamma_{poly} - \gamma_{w,poly} \tag{21}$$

$$W_{ww} = 2\,\gamma_w \tag{22}$$

W_{wp}, $W_{w,poly}$, and W_{ww} are the work of adhesion to the pigment, polymer, and the work of cohesion of water. γ_w is the surface energy of water and γ_p and γ_{poly} the surface energy of the pigment and the polymer. γ_{wp} and $\gamma_{w,poly}$ are the interaction energies at the water-pigment and water-polymer interfaces.

If the complex modulus is excessively high, then the polymer cannot deform within the time frame of the experiment (coalescing time) and, the second pathway, i.e., film rupture is followed. The determinate factor dictating which pathway the drying process will take can be likened to a chain with a weak link. The liquid film will crack if the $Q_{coalescence}$ is > than any or all of the dewetting terms (weak links), and conversely film formation will take place if all the dewetting terms are greater than the energy required for coalescence.

$$\text{Cracking if, } Q_{\text{coalescence}} > W_{ww}, W_{wp}, W_{wpoly} \tag{23}$$

$$\text{Filming if, } W_{ww}, W_{wp}, W_{wpoly} > Q_{\text{coalescence}} \tag{24}$$

$Q_{coalescence}$ is the ideal work required to consolidate the film to strain free, zero void film. Adhesion to the substrate and the complex shear modulus of the drying paint film are forces restraining complete coalescence. Consequently, if the rate of

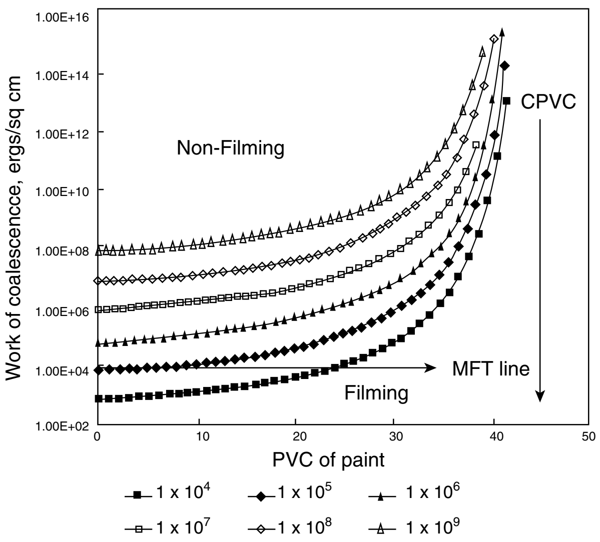

Figure 4—Model calculation of work of coalescence/cm^2 of a 3 mil dry film as a function of PVC, and the complex shear modulus of the binder polymer. Calculation assumes: Poisson's ratio = 0.425, spherical pigment particles and a CPVC of the pigment 46%.

evaporation of water is faster than the ability of the polymer to deform (compliance), strains and air inclusions develop. The air inclusions are micro voids that are filled with air that diffuses into the film as the water evaporates. Hence the volume change is always less than 1–K_c, but rather $\phi_{df} - K_c$. ϕ_{df} is the theoretical ratio of the specific volume of the film components to the actual specific volume of the dried film.*

$$sp \cdot vol_{strain\ free} = \sum_{n=i}^{n=m} \frac{\%_n}{\rho_n\, 100} \tag{25}$$

$$\phi_{df} = \frac{sp \cdot vol \cdot_{strain\ free}}{sp \cdot vol \cdot_{dried\ film}} \tag{26}$$

Poorly coalesced films are always cloudy or hazy because air inclusions or micro voids in the film cause a diffraction of transmitted light.† Conversely, well coalesced films are often crystal clear.

The complex shear modulus can be modified by polymer design and by the use of coalescing aids/filming aids, which act as a fugitive plasticizer to temporarily lower the complex shear modulus.

TEST OF THE MODEL

A good approximation of the Poisson's ratio for a filming polymer is ≈ 0.425 (the average of 0.5 and 0.35). If it is assumed that the critical packing constant, K_c, is ≈ 0.525 and the shape of the pigment particles are nearly spherical, *Figure* 2 shows a model calculation of the energy or work required for film formation at several moduli of the latex polymer. The MFT line represents a latex which will just form a film at 40°F. The model clearly shows the exacerbation of pigments and fillers on film formation. In the model calculation, the sign of the work is negative (indicating work done on the film), but for convenience of the log plot the absolute value of work is shown.

Methods of Measuring Film Formation

Both industrial and academic latex chemists and paint technologists have sought means of testing the film forming character of their experimental efforts. The most often determined property is the minimum filming temperature (MFT).

MFT is defined as the lowest temperature at which a coherent film will form. It is readily determined on a gradient temperature bar by visually observing the lowest temperature at which "clear" film can form. It is a measure of the temperature at which $Q_{coalescence}$, i.e., the product of volume change and the complex shear modulus/viscosity of the film equals or just exceeds the surface forces of the liquid phase. It is particularly useful on unpigmented systems. In simple copolymers and homopolymers, the ratio of MFT and T_g constant[20] is shown by equation (27).

$$\frac{MFT\ (K^{\circ})}{T_g\ (K^{\circ})} = 0.935 \tag{27}$$

Because the opacity of pigmented films confuses the observation of the coherency of the film, it does not accurately predict film coalescence of pigmented systems.

Film Stress Measurements

A more useful instrument for measuring film formation is the CGB instrument* described by Hoy and Peterson.[21] When a film forming composition is placed in the sample boat of the instrument (*Figure* 4), the initial response is a negative deflection due to the load placed on the beam. When ϕ is below critical packing, an excess of fluid maintains the fluidity of the dispersion and a positive deflection records only the weight loss. When critical packing is reached, the solid particles cannot move more closely together, i.e., free volume = 0. Thereafter, continued evaporative volume losses cause the

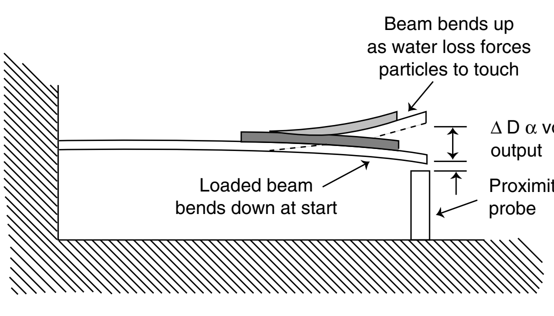

Figure 5—Schematic diagram of cantilevered gravimetric beam instrument (CGB).

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*Applies only to paints formulated below CPVC.

†Another cause of hazy or cloudy films is incompatibility with the surfactant system with the base polymer.

*Cantilever Beam instruments have been previously reported for measuring stress in coatings, see reference 3.

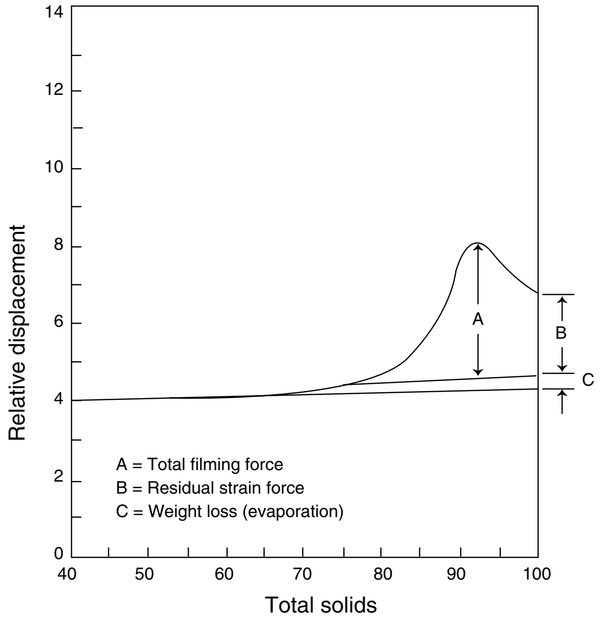

Figure 6—Measurement of film formation of an acrylic latex on the CGB instrument. The measurement was made at 25°C. MFT of the latex was 10°C.

surface forces to exert a tensile stress upon the bed of particles causing a rapid, pronounced deflection of the supporting beam (transverse strains). If the latex is a nonfilming composition, "mud cracking" takes place and the beam returns to the base line (localized strains); however, if the latex is a filming composition, the polymer deforms, flows, and encapsulates the pigment, i.e., the film coalesces. As the film forms, the stress on the beam is partially relieved and the deflection of the beam returns towards, but does not reach, the base line. The residual deflection of the beam is a measure of the residual transverse strain remaining in the film; the information that can be gained is: (1) the force required for polymer flow and deformation, $Q_{\text{coalescence}}$; (2) remaining excess strain in the film; and (3) volume solids at K_c (see *Figure* 5).

The information gained from this type of measurement together with the MFT provides the applications technologist with new perspective on polymer and formulation development. A polymer or formulation designed to relieve most of the stress of filming would have better adhesion, and be less prone to checking, cracking, and other performance defects.*

SUMMARY

A general model has been developed from thermodynamics for the work of film formation/unit area from latexes. The model is based on the product of volume changes that occur in the film subsequent to reaching critical packing and the modulus of the polymer as modified by pigment and fillers. The equation for the model is:

$$\frac{Q_{\text{coalescence}}}{\text{Area}_{\text{coating}}} = M^{*}_{\text{polymer}} \exp\left[\frac{f_{(\nu_1,\Xi)}\,\text{CPVC}}{\text{CPVC}-\text{PVC}}\right]\left[1-\frac{1}{K_c}\right]\left[t_{df}\left(1-\frac{\text{PVC}}{100}\right)\right]$$

The model predicts the effect of pigments and fillers on the filming properties of latex paint compositions and points to research areas in which technical improvements need to be made. It is hoped that the model will promote a better understanding of the filming process and will assist both latex polymer synthesis and coating application technologists in their quest to develop better products.

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*As a general rule, baked films usually outperform films formed at room temperature. It is the author's belief that transverse and local stress reduction is largely responsible for the better performance. Baked films should contain only the stress induced by the cooling process. Ideally a baked film having the same thermal expansion coefficient as the substrate would provide the best adhesive performance.