'Mud-cracking' in a Latex paint film

ICI Technology

1 The drying process of liquid paint

Decorative latex paints consist mainly of polymer latex, titanium dioxide pigment (TiO_2) and water. In the past, coalescing solvents were used which plasticise the latex and improve its flow, but nowadays the pressure is on to produce paints free of such organic solvents. Mineral extenders such as chalk, clay and talc are frequently added. As well as reducing the price of production, the extenders alter the colour and the opacity of the paint, in particular since their inclusion ensures that air will be incorporated during drying. At the so-called critical pigment volume concentration (cpvc) there is just enough latex to encapsulate fully the TiO_2 and extender. (The term cpvc is therefore somewhat misleading, as it is more like a critical latex volume concentration, but it really depends on the mixture of different types of extender, pigment and latex.) Beyond cpvc air is entrained, and failure in terms of cracking is observed in the drying film. The nucleation of the cracks is at an edge or at an imperfection (for example an air bubble).

We now briefly review some of the behaviour inferred from existing experimental work.

- Thicker coatings are more likely to show cracking.
- Paints without organic solvent are more likely to show cracking.
- The use of talc (whose particles have the shape of platelets) as the main extender reduces cracking.
- Different substrates (e.g. greased) exhibit different cracking.
- The rate of water transport (e.g. porous substrates) effects the cracking.
- Low humidity and low temperature (below the paint's film formation temperature) lead to micro-cracking.
- At cpvc, the stresses in the film seem to reach a maximum.

To explain these phenomena it was viewed as crucial to understand how stresses could build up within the paint layer, since this causes the crack-initiation. It was noted, however, that ICI is not interested in a study on the crack-propagation, but rather in avoiding cracks being initiated altogether.

A comparison was made with mud-cracking and, to get a better understanding of the difference between mud and paint, experiments were performed during the week of the Study Group, using cornflour (starch) as a substitute for latex and talcum powder for extender. The idea is that pure extender behaves like mud: when drying, it always shows mud-cracking and when fully dry, it returns to its original granular form. The starch, although not a very good binder, exhibits large cracks in thick films and micro-cracks in thinner films, and also remains rather more coherent when dry. The ICI paint, having been carefully developed through experimental work, was never observed to crack.

The general belief at the Study Group was that the dominant mechanism for water drainage in mud is different from that in paint. Although in both the water extracted by evaporation at the free surface, the drainage in mud is by capillary pressure, while in paints after some time a skin or gel-film is formed at the surface, and thereafter the drainage is diffusion-driven. For drying mud an elastic model is used to quantify the stress build-up due to shrinkage by water loss; cracks are assumed to initiate if and when the failure stress is reached. Unfortunately, such a simple model fails to capture the difference between thick and thin paint films. This ties in with the observation that pure-extender films always exhibit cracking, regardless of thickness.

In paint the latex polymer is believed to make a sort of network during the drying process, by entanglement between latex particles and also by binding to the TiO_2 and to the extenders. This is referred to as a coalescence process in the literature.

In this report, we discuss possible models for the stress build-up in the paint layer. Since the visco-elastic properties of the paint during the drying process are not known, it is difficult to draw any definite conclusions from the models suggested. If, as seems likely, during the film formation there is a large change in the elastic properties and/or permeability of the material, then the models may well predict the difference between thin and thick paint layers. They will also predict that the cracking is less for particular extenders if the relaxation in the resulting viscoelastic material is faster.

2 Water movement

2.1 Capillary drainage in mud

Because of the possible similarity with cracking in mud the modelling ideas used in this area should be reviewed. In addition the mechanisms are probably relevant to the early stages of paint drying. One useful source of experimental data is Allain & Limat (1995) who examined cracking using experiments on an aqueous colloidal silica suspension.

2.2 Consolidation

An important question during this part of the process is whether the drag force exerted by the water as it moves through the matrix of extender, latex and pigment can compact the matrix. The effect of the compaction would be to deform and spread the latex droplets onto the extender particles before any irreversible curing of the latex occurred.

A model for the removal of water by evaporation and the resultant consolidation is to assume that the water moves in a deforming porous matrix according to Darcy's law. The coordinate system is fixed in space, and the porosity and velocity of the matrix are denoted by ϕ and w_m respectively. Conservation of matrix implies that in one dimension we have

$$\frac{\partial \phi}{\partial t} = \frac{\partial w_m}{\partial z}.$$

Darcy's law says that the velocity w of the water through the matrix is driven by the pressure gradient:

$$w - w_m = k\frac{\partial p}{\partial z}.$$

Here k is the permeability of the matrix which will be a function of the porosity.

Now we imagine there are two mechanisms deforming the matrix. First there is the random motion of the particles, which will be the dominant mechanism while the matrix particles are at low density (high porosity). However, as the matrix particles begin to contact each other the particles will deform due to the stresses produced by the flowing water.

Rather than derive a model equation for the matrix we make some order-of-magnitude estimates of the available forces. The water will experience a pressure equal to the surface tension pressure, while the adjoining matrix particles will experience atmospheric pressure. Hence the maximum available pressure drop is

$$\Delta p_{max} \approx \frac{\gamma}{R_E}$$

where γ is the surface tension of water and we estimate the curvature of the meniscus by using the extender particle radius R_E. An important question is whether the Darcy drag during the removal of water by evaporation at the surface during this phase causes any appreciable deformation of the latex drops. We assume that the maximum pressure drop occurs through a paint layer of thickness d (note this layer will typically be the thickness of the drying skin formed on the paint as this is the dominant source of pressure drop). The resulting stress causes the latex to deform by viscous flow, and we can estimate the rate of deformation in the latex by assuming

$$\frac{\mu_L w_m}{R_L^2} \approx \frac{\Delta p}{d},$$

with R_L the latex particle radius. It remains to find reliable estimates for the latex viscosity, however. This expression will indicate if the expected deformation is important.

A second important question is how strong the diffusion of particles away from the drying surface is compared to the Darcy drag force. In particular if diffusion is small then there will be a compacted region formed at the upper surface, with paint – in its applied state – underneath it. If we take the evaporation rate (m/s) from the surface to be v then the question is the relative size of this to any diffusion of the particles. Taking the diffusion of paint particles in water to be D_p we should compare D_p/d with v.

Once the surface skin has formed at some point, the Darcy drag will be large enough that the capillary pressure cannot pull the water through the layer. Then, the water surface will recede into the matrix, leaving behind extender particles, wet latex and pigment. Using the estimate for the maximum pressure drop we may get an idea for the maximum layer thickness from

$$d_{max} = \frac{k\gamma}{vR_E}$$

where v is the velocity of water driven by the process of evaporation. At this point, either the consolidated region extends to the bottom surface, or it does not.

The latex in the dry part of the consolidated layer will start to undergo the irreversible reaction that interlaces the molecules. As this happens, we assume that the layer becomes more elastic and is able to support some stress.

2.3 Diffusion and evaporation model

We now consider the case where the advective flow of the water is negligible so the process is diffusion driven. The main purpose of this section is to derive the governing equations when the volume fractions of the various species are all of similar magnitude. Now ϕ denotes the volume fraction of water and ϕ_s that of the solid particles. So, assuming there are no voids or air gaps, $\phi + \phi_s = 1$ and $\phi/V_w + \phi_s/V_s = c$, where V_w, V_s are the molar volumes and c is the total concentration, $c = c_w + c_s$, in moles per unit volume. Fick's law gives the volume fluxes as

$$\mathbf{J}_w = -c\left(D_{ww}\nabla\phi/c + D_{ws}\nabla\phi_s/c\right), \quad \mathbf{J}_s = -c\left(D_{sw}\nabla\phi/c + D_{ss}\nabla\phi_s/c\right).$$

The Fickian diffusion coefficients may be functions of ϕ, ϕ_s, and also of pressure and temperature. We neglect the latter effects and write $D_{ij}(\phi)$. Conservation of water and of solids (when there is no air incorporated) then implies that these volume fluxes must add up to zero. Writing $\alpha = V_w/V_s$, Fick's law reduces to

$$\frac{\partial\phi}{\partial t} = \nabla\cdot(D(\phi)\nabla\phi), \tag{1}$$

where

$$D(\phi) = \frac{(D_{ww}(\phi) - D_{ws}(\phi))\alpha}{\phi(1-\alpha)+\alpha}$$

is a non-negative diffusion coefficient. It is this coefficient, and its dependency on ϕ, that is important in the model rather than the details of the various D_{ij}.

To this equation we need to apply boundary conditions. If we consider the simple one-dimensional problem within the region $0 \le z \le h(t)$ then the condition on the bottom surface requires no flux of water (or solid) so that

$$\phi_z = 0 \text{ on } z = 0.$$

The upper surface is a free boundary and needs two conditions. These are given by ensuring that no solids escape from the surface and that the water flux is a specified evaporation rate v. Hence

$$J_w + (1-\phi)h_t = 0 \quad \text{and} \quad J_w - \phi h_t = v \quad \text{at } z = h(t).$$

Note that this simply implies that h is given as a time integral of v. The full problem is then specified by giving an initial paint thickness and water distribution.

2.4 Stress-driven diffusion

In the polymer literature (penetration of liquids in polymer material) it is noted that the stresses in the gel-like material of the film squeeze out the water, a phenomenon called stress-driven, non-Fickian or case II diffusion. This means that the diffusion is in effect time-dependent, as it depends on the relaxation of the polymeric species. It is assumed that the stress build-up and relaxation are dictated by a Maxwell equation (see also section 3). In one space dimension, this gives the following system of equations for the volume fraction ϕ, the layer thickness h, and the horizontal stress component $\sigma = \sigma_{11}$:

$$\begin{array}{ll}
\phi_t = (D(\phi)\phi_z)_z + (\kappa(\phi)\sigma_z)_z & \text{for } 0 < z < h(t),\ t > 0, \\
\sigma_t = g(\phi, \phi_t) - \beta(\phi, \phi_t)\sigma & \text{for } 0 < z < h(t),\ t > 0, \\
D(\phi)\phi_z + \kappa(\phi)\sigma_z = 0 & \text{for } z = 0,\ t > 0, \\
D(\phi)\phi_z + \kappa(\phi)\sigma_z = -K\phi(1-\phi) & \text{for } z = h(t),\ t > 0, \\
h_t = -K\phi \ \text{ with } \ h(0) = h_0 & \text{for } z = h(t),\ t > 0, \\
\phi = \phi_0(z) \ \text{ and } \ \sigma = 0 & \text{for } 0 \le z \le h_0,\ t = 0.
\end{array} \tag{2}$$

Here D is the diffusion coefficient, κ is related to the porosity, and K is the evaporation constant, with the evaporation given by $K\phi(h(t), t)$. For g and β we refer to section 3.

Conditions on the initial data are

$$0 \le \phi_0 \le 1, \quad \text{and} \quad h_0 > 0.$$

If the evaporation is very fast, in the limit $K \to \infty$, the boundary conditions at $z = h(t)$ reduce formally to

$$\phi = 0, \quad \text{and} \quad h_t = D(\phi)\phi_z + \kappa(\phi)\sigma_z.$$

These so-called Stefan conditions correspond to a negative latent heat. Writing $\varepsilon = 1/K$, the condition resembles the kinetic condition in generalised Stefan problems, apart from the factor $(1 - \phi)$.

In using this model it is necessary to determine the diffusion coefficient $D(\phi)$. One common choice is a Heavyside function to account for the transition from a glass to a rubber phase. However, although materials that perform this transition often show a drop in the diffusion coefficient, literature on solvent diffusivities in gelling solutions is scarce.

3 Stress-build up

Since the crucial point of this analysis is to determine how paint mixtures might be altered to reduce the occurrence of cracking, it is necessary to model the increases in stress that might cause fracture within the drying paint layer.

The classical approach, and that used in cracking of mud, is to assume that as water is removed from the layer the paint shrinks and that this shrinkage is isotropic. If in addition we assume that the drying paint layer acts as an elastic material then the model used is identical to that for thermo-elasticity with water content assuming the role of temperature. This model assumes that the material acts elastically and therefore, for a paint, might be a reasonable approximation when the particles become rather close packed.

3.1 Thermo-elasticity

For a thin layer of mud or paint we couple the equations for the stress in linear elasticity with the variation in water volume in the following way. Consider a unit volume $V(\phi_0)$ of paint in an unstressed state with initial water fraction ϕ_0. For this to change to a volume $V(\phi)$, while remaining unstressed, as the water content changes we have

$$\operatorname{div}\mathbf{u} = V(\phi) - V(\phi_0),$$

where $\mathbf{u} = (u, v, w)$ is the displacement field of the solid matrix. Hence, assuming that the change is isotropic and that the internal stress due to the variation in water volume is $2\mu\operatorname{div}\mathbf{u} = A(\phi) = \alpha(\phi - \phi_0)$, the stress tensor takes the form

$$\sigma = \begin{pmatrix} \lambda\operatorname{div}\mathbf{u} + 2\mu u_x + A & \mu(u_y + v_x) & \mu(u_z + w_x) \\ \mu(u_y + v_x) & \lambda\operatorname{div}\mathbf{u} + 2\mu v_y + A & \mu(v_z + w_y) \\ \mu(u_z + w_x) & \mu(v_z + w_y) & \lambda\operatorname{div}\mathbf{u} + 2\mu w_z + A \end{pmatrix}.$$

Here the elastic coefficients, λ and μ may depend strongly on ϕ. Boundary conditions are

$$\begin{array}{ll} \text{no slip at the substrate } z = 0, & u = v = w = 0, \\ \text{stress free at the surface } z = h, & u_z + w_x = 0, \quad v_z + w_y = 0 \\ & \lambda(u_x + v_y + w_z) + 2\mu w_z + \alpha(\phi - \phi_0) = 0. \end{array}$$

Balancing the forces then imposes the equation div $\sigma = 0$ and this then gives the dependence of the stress upon the water content.

If we apply thin layer scales (scaling z and w with the aspect ratio, thickness over typical length scale), the leading-order equations for σ reduce to

$$u_{zz} = 0, \quad u = 0 \text{ at } z = 0, \quad u_z = 0 \text{ at } z = h,$$

$$v_{zz} = 0, \quad v = 0 \text{ at } z = 0, \quad v_z = 0 \text{ at } z = h,$$

$$(\lambda + 2\mu)(u_{xz} + v_{yz} + w_{zz}) + \alpha\phi_z = 0,$$

$$w = 0 \text{ at } z = 0, \quad \lambda(u_x + v_y + w_z) + 2\mu w_z + \alpha(\phi - \phi_0) = 0 \text{ at } z = h,$$

so that, to leading order,

$$u = 0, \quad v = 0, \quad (\lambda + 2\mu)w_z + \alpha(\phi - \phi_0) = 0.$$

We find the stresses to be

$$\sigma_{11} = \sigma_{22} = \frac{2\mu}{\lambda + 2\mu}\alpha(\phi - \phi_0),$$

$$\sigma_{12} = \sigma_{13} = \sigma_{23} = \sigma_{33} = 0.$$

In this derivation the 'thermo-dynamical' term $\alpha(\phi - \phi_0)$ may be replaced by a general function $A(\phi)$, with $A(\phi_0) = 0$ if the mud is unstressed initially. For the paint we will extend the idea of tensile stress to a visco-elastic model.

If data is available concerning the elastic properties of the paint film as it dries it would be possible to perform a numerical simulation using nonlinear spring elements whose properties depend on the local water content. Such simulations would be relatively straightforward.

3.2 Shrinkage of paint

The previous subsection discussed stress build-up in a homogeneous shrinking elastic material. These ideas need to be extended to the case of a paint where there are (at least) two solid components, only one of which (latex) shrinks. We discuss a simple model for a uniform region of paint. We use the volume fractions for water, latex and pigment, $\phi + \phi_l + \phi_p = 1$, so that the volume of solids is given by $(\phi_l + \phi_p)V$, where $V(t)$ is the total volume at time t. Although the total volume changes in time due to water evaporation, the volume of solids must remain constant, and hence

$$V(\infty) = (1 - \phi(0))V(0), \quad V(t) = \frac{(1 - \phi(0))V(0)}{1 - \phi(t)}.$$

The volume change from time t_0 to t_1 is related to

$$\gamma^3 = \frac{V_1}{V_0} = \frac{1 - \phi_w(t_0)}{1 - \phi_w(t_1)}.$$

Assuming the region is confined by a surface so that it cannot shrink laterally, an estimate for the resulting linear strain components is given by $1 - \gamma$. This supplies us with the maximal strain due to water loss as $t \to \infty$, e.g.

$$\varepsilon_{11} = 1 - (1 - \phi(0))^{1/3} = 1 - (\phi_l(0) + \phi_p(0))^{1/3}.$$

It is not clear how the stress amplification factor depends on the mixture of latex and pigment; Toussaint (1973/74) argues that

$$\sigma_{11} = 2E\frac{1 - (\phi_l + \phi_p)^{1/3}}{1 - \phi_p^{1/3}},$$

when the elastic modulus E of the latex is much lower than that of the pigment; if the moduli are almost equal, $\sigma_{11} = 2E\varepsilon_{11}$.

3.3 Failure criteria

If the available models can predict the stresses within the layer then it is necessary to determine some criteria for the failure of the material and hence the initiation of a crack. Classical Griffith crack theory uses the concept of a critical stress intensity or failure stress. If we denote the critical stress intensity factor for the paint by K_{ic}, then the so-called fracture stress, required to develop a fracture from a flaw with a given initial size R is given by $\sigma = \frac{K_{ic}}{\sqrt{\pi R}}$. For the paint layer we might expect R same order as the typical particle size R_E.

One other possible failure criteria is that the paint's elastic properties are nonlinear. In this case if the material softens sufficiently quickly then there will be a natural tendency to tear. Such behaviour would become apparent if the stress-strain relationship of drying paint were more completely known.

3.4 Viscoelastic stresses

We now generalise the horizontal stress in the layer as derived from the thermoelasticity model to allow for viscoelastic effects. We assume that only the tensile stresses σ_{11} and σ_{22} are important. The viscoelastic relation for $\sigma(z,t) = \sigma_{11} = \sigma_{22}$ is assumed to be given by an hereditary integral equation (Boltzmann or Maxwell equation):

$$\sigma(z,t) = \int_0^t \exp\left\{-\int_\tau^t \beta\left(\phi(z,s), z, s\right)\, ds\right\} g\left(\phi(z,\tau), z, \tau\right)\, d\tau. \qquad (3)$$

Here it is assumed that $\sigma = 0$ at $t = 0$, starting initially with an unstressed state. In general the functions β and g may also depend on derivatives of ϕ. The function β is related to the relaxation time of the polymer solution, $\beta = 1/\tau_s$, while g depends on the viscoelastic model that is used for the material. By differentiating with respect to time, we find the more familiar differential form

$$\frac{\partial \sigma}{\partial t} + \beta(\phi, z, t)\sigma = g(\phi, z, t). \qquad (4)$$

For example, a Maxwell element consists of a spring with Young's modulus $E(\phi)$ and a dashpot with viscosity $\eta(\phi)$ in series, for which:

$$g(\phi, \phi_t) = E(\phi)\dot{\gamma}, \quad \beta(\phi, \phi_t) = \frac{E(\phi)}{\eta(\phi)} - \frac{E'(\phi)\phi_t}{E(\phi)}. \qquad (5)$$

The strain rate $\dot{\gamma}$ in (5) represents the rate of swelling or shrinking. Alternatively, other viscoelastic models that could be used include the Jeffrey-element, Voigt-Kelvin or the Oldroyd-B model, consisting of different systems of springs and dash-pots. We remark that without experimental data on the material properties it is not possible to determine the functional behaviour of the coefficients. Scaling laws have been derived for different stages in the polymer dissolution process by, for instance, Brochard and De Gennes (1983). Such scaling laws could be incorporated by choosing the functional forms of the coefficients properly.

There was some discussion as to whether shrinkage was the dominant source of stress within the paint layer. One possible additional source might be an tendency of latex particles to entangle creating tensile stresses as the latex cures. No data was available to determine if this was important.

4 Latex reactions

There was considerable discussion concerning the processes by which the latex cures. It is known that Latex molecules deform (i.e. they flow, distort and bind) due to the stress (above the critical glass temperature) and this deformation takes time. When the paint layer is dried too quickly (for example at very low humidity) it is possible that the lack of time to distort may create a weak structure and hence increase the likelihood of cracking (this was briefly discussed in section 2.2). Alternatively the binding may be the limiting step, in which case the cracking would be unrelated to the critical glass temperature. In Cairncross, Francis & Scriven (1996) the rate of gel formation is taken into account by coupling the diffusion equation for the evaporating water (and possibly other solvents) to a chemical reaction that models the formation of a gel or skin.

The idea of a reaction-based model for the binding was considered. If we denote the molar concentrations of latex and extender by L and E respectively, then the gel formation process might crudely be modelled by a reaction of the form

$$LH_2O + nE \to LE_n + H_2O.$$

Here LH_2O represents latex in solution and LE_n the gel, which is a combination of latex and extender. The relative concentrations of latex and extender in the paint under consideration determine the parameter n. We can expect the constitutive properties of the gel to depend crucially on n.

An alternative approach to the modelling of latex entanglement is to use a phase change model, with an order parameter representing the degree of entanglement. Such a model would be analogous to those developed as phase-field models of solidification.

5 Conclusions

A number of possible physical phenomena have been proposed that may explain the observed tendency for paints to crack. There is, as yet, insufficient experimental data to fit these models or to determine which might be the dominant mechanism.

The following points are still unclear or need to be considered in more detail.

- Local variation in composition: it was suggested that above cpvc the different solid particles may segregate. The migration of solid particles may be an additional cause of tensile stresses or create weak points to initiate cracks.

- Air gaps: above cpvc, air is enclosed in the paint layer, creating a brittle, porous material. It is likely that when there is not sufficient latex around, no strong film or skin can be produced and the drying may be due to a combination of capillary pressure and diffusion.

- Packing of solids: good or bad packing of solids may be important in the entrapment of air or creation of voids.

- The fact that thick layers are more likely to crack seemed to be contradicted by simple intuition. This observation that thick films behave differently from thin films may simply be an effect of different time scales for evaporation and diffusion. Denoting by h the (original) thickness of the film, K the rate of evaporation constant, D the (typical) diffusion coefficient, then the two time scales are

  $$t_1 = \frac{h}{K}, \quad t_2 = \frac{h^2}{D}.$$

  We observe that larger h or larger K corresponds to faster evaporation in relation to the drainage by diffusion, so that it is more likely that a "dry-ish" film forms with a wet paint layer underneath. When large stresses develop in the dry film and the relaxation is too slow, cracks will appear.

References

C. Allain and L. Limat, Regular patterns of cracks formed by directional drying of a colloidal suspension, *Phys. Rev. Letters* 74:2981-2984, 1995.

F. Brochard and P.G. de Gennes, Kinetics of polymer dissolution, *PhysicoChemical Hydrodynamics* 4:313-322, 1983.

R.A. Cairncross, L.F. Francis and L.E. Scriven, Predicting drying in coatings that react and gel: drying regime maps, *AIChE Journal* 42:55-67, 1996.

A. Toussaint, Influence of pigmentation on the mechanical properties of paint films, *Progress in Organic coatings* 2:237-267, 1973/74.

Contributors

Many people worked on this problem, including Jon Chapman, Don Drew, Barbera van de Fliert, Jens Gravesen, Michael Grinfeld, Poul Hjorth, Rein van der Hout, Peter Howell, Sam Howison, Chris Howls, Brian Kemish, John King, L. Mahadevan, John Ockendon, Colin Please, Giles Richardson, Neil Stringfellow, John Byatt-Smyth, Jonathan Wattis, Wei Wendy Zhang.

Study Group Report by BvdF and CPP.