

# Drying of Water-based Paints

## 1. Introduction

Courtaulds had proposed to ask the Study Group to model the evaporation from a water-based paint and determine whether it can be optimised by a suitable distribution of sizes of the suspended paint droplets. Though the problem was withdrawn formally, it did receive some attention from the Study Group participants.

The paint that the group was asked to consider is an emulsion of spherical paint droplets in water, which is sterically stabilised by surfactant. The initial volume concentration of paint is about 33% and the typical droplet diameter is  $2a = 200$  nm. The paint dries rapidly to ‘touch-dry’ for of order  $10^3$  s (15 minutes) and then more slowly for of order  $10^5$  s (1 day). The paint layer is 10 microns thick corresponding to a packed layer of about 50 paint droplets deep, though it should be noted that the droplets coalesce when forced sufficiently close together.

## 2. Four-stage model

Based on the above observations, a four-stage model of drying was developed.

### *Stage 1: Freely moving droplets*

Initially the droplets are not in contact and are relatively free to move around in the suspending fluid (figure 1a). The Brownian diffusion coefficient for a droplet is  $D_B = kT/6\pi\mu a$ , where  $k$  is Boltzmann’s constant,  $T = 300$  K is the absolute temperature,  $\mu = 10^{-3}$  Pa s is the viscosity of water and  $a$  is the droplet radius. For the parameters given  $D_B \approx 1.5 \times 10^{-12}$  m<sup>2</sup>s<sup>-1</sup>, and so the droplet can diffuse through its own radius in of order  $a^2/D_B = 10^{-2}$ s. This is much less than the initial drying time, which suggests that the droplets will be able to jiggle into a well-packed configuration as evaporation proceeds and the volume fraction of paint increases. During this phase, the evaporation rate is roughly constant and governed by the rate of transport of vapour away from the paint/air interface, and hence by the ambient temperature, humidity and ventilation of the air.

### *Stage 2: Squashing of a packed layer*

A second stage is entered when sufficient water has been evaporated to leave a well-packed bed of paint droplets between which is a porous network of drainage channels occupied by water (figure 1b). The air/fluid interface is no longer flat due to protrusion of the topmost layer of paint droplets through the receding aqueous layer. The curved interfaces at the air/fluid boundary increase the pressure in the packed droplets and decrease the pressure in the aqueous phase, thus causing the droplets to squash together and deform against the restoring action of the paint/water surface tension. The squashing of the packed layer squeezes water out of the pore space towards the surface layer and reduces the curvature of the air/fluid interfaces.

An important question to address is whether the movement of water through the porous network is the rate-determining process in this stage, since if it were then the optimal strategy for creating a fast drying paint would be to maximise the permeability of the packed bed by having roughly equally-sized droplets (so little droplets don’t clog up the channels between the big droplets). This turns out **not** to be the case. The differential stresses due to the curvature of the free surface are of order  $\Delta P = 7 \times 10^5$  Pa (based on surface tension  $0.07$  Nm<sup>-1</sup> and radius of curvature  $100$  nm). A pressure gradient  $\Delta P/L$ , where  $L = 10^{-5}$ m is the

depth of the layer, would drive fluid through a porous network of typical channel radius  $\delta$  at a velocity of order  $\delta^2(\Delta P/L)/\mu$ . Thus fluid could escape through the depth of the layer within a timescale of  $10^3$ s if the channel radius were larger than  $(\mu L^2/10^3\Delta P)^{1/2} = 10^{-11}$ m. Since the channels between the paint droplets are very much larger than this, we conclude that **the pressure drop associated with the movement of water through the porous network is negligible.**

The stresses associated with the deformation of the visco-elastic polymer in the interior of the droplet are also negligible since the strain rate is no more than  $10^{-3}\text{s}^{-1}$ . Hence, as discussed further in section 3, the configuration of the paint droplets at any instant is a static equilibrium in which the paint/water surface tension is balanced by a uniform pressure difference between the paint and the water.

In this stage the rate of evaporation is proportional to the surface wetted area and slowly decreases as the water meniscii are sucked further down the throats between the top layer of droplets.

#### *Stage 3: Coalescence and inversion*

As evaporation proceeds the droplets are pressed ever more firmly together. If the droplets do not coalesce then the water meniscii will be sucked completely through the topmost throats, air enters the paint layer and the subsequent drying is analogous to the drying of a partially saturated sand-pack. Air in the paint is clearly undesirable and so the polymer rigidity should be such that the droplets coalesce before this happens. The simplest criterion for modelling coalescence is that the pressure between the droplets rises to a critical value dependent on the surfactant concentration (though there may also be a rate-dependence if the surfactant redistributes itself along the surface of the droplet). On coalescence the emulsion inverts to become water droplets in polymer rather than polymer droplets in water (figure 1c). Some water will be expelled to the air-interface by the rearrangement of the emulsion and evaporated rapidly but most will be trapped.

#### *Stage 4: Diffusion of remnant water*

Finally, the trapped water must diffuse slowly through the paint layer (figure 1d). A total drying time of  $10^5$ s can be achieved by a diffusion coefficient for water in polymer of order  $L^2/10^5 = 10^{-15}\text{m}^2\text{s}^{-1}$ . This coefficient could be measured if it is not already known. A mathematical model of this final stage is given by

$$\begin{aligned} \frac{\partial C}{\partial t} &= \frac{\partial}{\partial z} \left( D(C) \frac{\partial C}{\partial z} \right) && \text{(diffusion eqn.)} \\ C(L, t) &= 0 && \text{(rapid evaporation at surface)} \\ \frac{\partial C}{\partial z} \Big|_{z=0} &= 0 && \text{(no flux at lower boundary)} \end{aligned}$$

where  $C$  is the concentration of remnant water, the paint layer occupies  $0 < z < L$  and  $D(C)$  is the diffusion coefficient, which probably decreases as  $C$  decreases and the paint becomes more hydrophobic (and possibly 'cured'?). In this stage the rate of evaporation is determined by diffusion of water through the layer to the air interface.

#### *Comparison with experiments*

This four-stage model is consistent with experimental data provide by John Newbury for the drying of another suspension (figure 2). A period of constant rapid evaporation (stage 1) was followed by a period of decreasing evaporation (stage 2), a little burst of evaporation (stage 3) and then a final slow drying (stage 4).

### 3. Paint performance and modelling

#### *Optimal packing*

If all the droplets are the same size then they will jiggle into a hexagonally close-packed configuration with a paint fraction of about 74% (figure 3). In this packing half the pores are surrounded by an octahedron of 6 droplets and could accommodate a smaller sphere of radius  $(\sqrt{2}-1)a = 0.41a$ ; the other half are surrounded by a tetrahedron of 4 droplets and could accommodate a smaller sphere of radius  $(\sqrt{3/2}-1)a = 0.22a$ ; the throats will allow the passage of a sphere of radius  $(\sqrt{4/3}-1)a = 0.15a$ .

These observations suggest that the rapid drying stage (stage 1) could be extended to larger paint fractions than 74% by adding some smaller droplets. While it is tempting to add medium-sized spheres (e.g.  $0.22a$ ) to fill up the pores, there is a danger that, because they are too large to traverse the throats, several might get stuck in one pore causing disruption to the basic close-packed lattice and doing more harm than good. It thus seems a better idea to add a larger number of smaller droplets ( $\leq 0.15a$ ) to fill up both pores and throats. If it is assumed that smaller spheres could occupy 64% (random packing) of the 26% space in the basic lattice then the total packed fraction would rise to 91%. Empirical evidence from the packing of kettle elements (John Newbury) suggests that, due to inefficiencies in packing, it may be better to use a 3:7 ratio by volume of  $(a/7)$ -spheres to  $a$ -spheres.

While the exact mix probably needs to be determined experimentally (or by simulation of Brownian sphere packing on computer), it is clear that more water can be got out quickly by having a bidisperse paint with the ratio of large to small droplet radii of at least 7:1.

#### *Optimal squashing*

If the paint is monodisperse then the difference in pressure  $\Delta P_{pw}$  between the paint droplets and the interstitial water starts at  $2\gamma_{pw}/a$ , where  $\gamma_{pw}$  is the paint/water interfacial tension. As  $\Delta P_{pw}$  increases, the droplets are squashed together and the radii of curvature of the paint/water menisci satisfy

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{\Delta P_{pw}}{\gamma_{pw}}, \quad (1)$$

where the right-hand side is a slowly varying function of time. For each value of  $\Delta P_{pw}$ , solution of (1) (an exercise in 3D numerical geometry) gives the equilibrium configuration of the interior of the packed bed and hence we could derive a relationship between the residual porosity and  $\Delta P_{pw}$ . (Such calculations have been made by geologists interested in partially molten rocks. One reference is von Bargen & Waff, *Journal of Geophysical Research*, v.91, p.9261, 1986, but the most comprehensive study has been done by Mike Cheadle, now a lecturer in the Department of Earth Sciences at Liverpool University.)

Each value of  $\Delta P_{pw}$  also corresponds to an equilibrium position of the water/air meniscus in the throats of the topmost layer (another exercise in 3D numerical geometry), and hence to an area of exposed water and an evaporation rate. The evaporation rate could then be linked to the changes in the residual porosity in the underlying squashed bed. Numerical calculations would identify: (1) the rate of change of porosity with time and (2) the critical value of  $\Delta P_{pw}$  at which the water menisci are sucked through the topmost throats.

If the paint were polydisperse then the small paint droplets would be relatively undeformable, the bed would be less squashy and stage 3 (inversion) would be reached with relatively little drying in stage 2 (squashing). Inversion would occur at comparable inter-droplet pressures to before and so the effect of polydispersion is to extend stage 1 at the expense of stage 2.

### *Optimal inversion*

It is clear from the above that the surfactant should be chosen to be sufficiently strong that the suspension does not invert prematurely, truncating the squashing stage and trapping water for the slow diffusional stage 4. However the surfactant should not be so strong that air is sucked into the paint. The optimum choice of surfactant depends on the three surface tensions (air/water, air/paint and water/paint) and the coalescence criterion. Some modelling thought should also be given to whether coalescence of two droplets triggers coalescence of neighbouring droplets and whether the surface layer of droplets will coalesce at the same time as the underlying layers.

#### **4. Further comments**

While various theoretical calculations could be pursued for idealised or random packed-bed geometries, it seems more sensible to investigate the qualitative features of this model experimentally by making measurements of the evaporation rate and residual water content as functions of time. If the four stages can be identified (as in John Newbury's experiments) then quantitative measurements can be used to identify the packing fraction, squashability, inversion criterion and diffusion coefficient for a range of emulsions and optimise the performance. Using a microbalance is probably the simplest way of measuring drying rates, but electrical measurements, such as the resistance or capacitance of the paint layer, may be more sensitive.

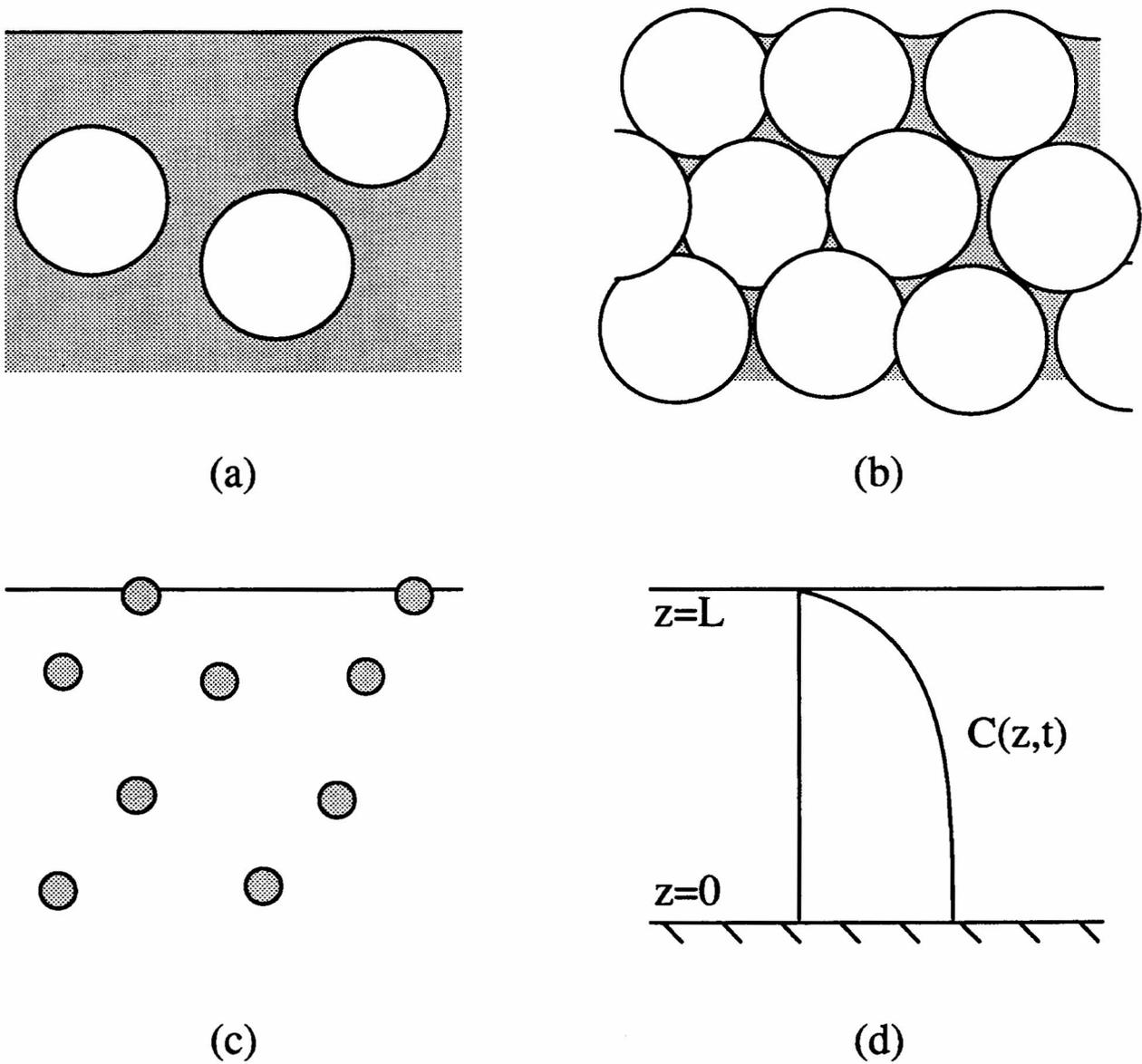


FIG. 1 The four-stage model drying process: (a) Paint droplets are separate and free to move; (b) Paint droplets in packed configuration. Curvature of the interfaces with air presses the droplets together as the water/air meniscus slowly retreats down the topmost throats; (c) Droplets coalesce and emulsion inverts; (d) Diffusion slowly removes remnant water.

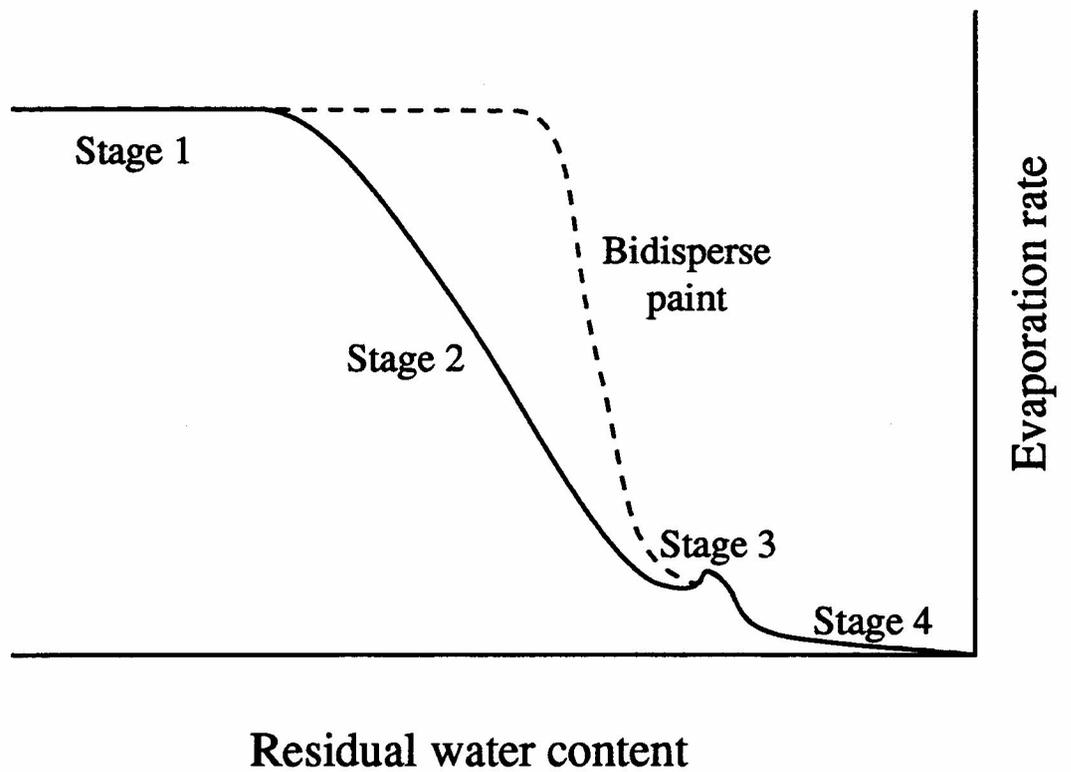


FIG. 2 Schematic of experimental data provided by John Newbury. The qualitative regions of the curve are identified with the four-stage drying model as shown. Addition of some smaller paint particles extends stage 1 at the expense of stage 2 (dashed curve).

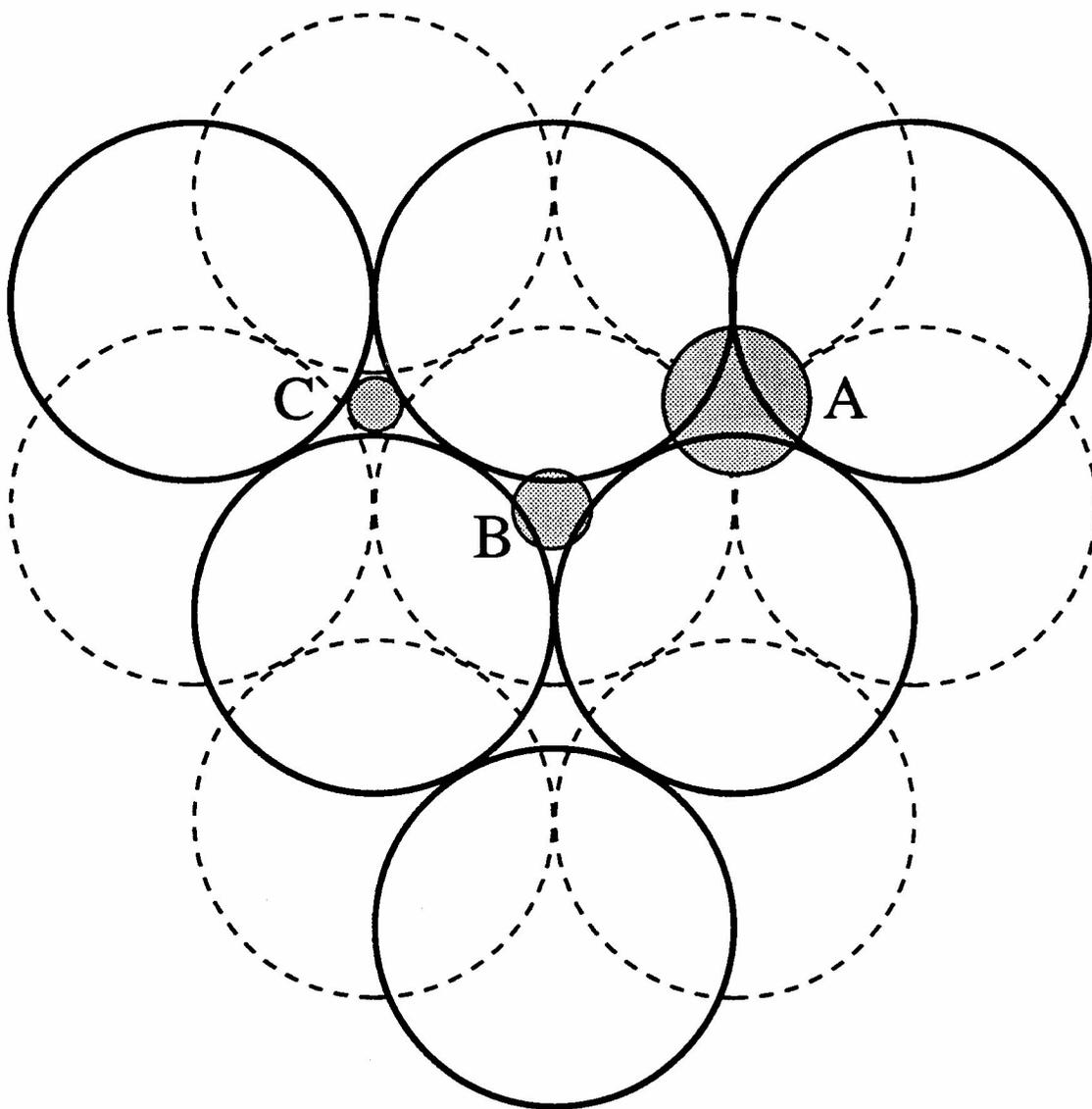


FIG. 3 Two layers of a hexagonal close-packed lattice (solid and dashed circles) showing large pore (A), medium pore (B) and throat (C) between the layers (shaded circles).