

DRYING AND CURING OF STAINS AND LACQUERS USED IN FURNITURE FINISHING

Y.M. Stokes¹ and P. Pendleton²

1. Problem description

Nexus Pty Ltd is a furniture manufacturing company that has been operating for 25 years at Victor Harbor in South Australia and currently employs 70 people. It supplies Australian furniture retailers and also exports a small amount of product to New Zealand and Japan. A variety of items of furniture are made, mostly from pine. The furniture is finished with a stain and two lacquer coatings which give it a semi-gloss surface.

In 1997 Nexus engaged a consultant to design a semi-automated finishing line, so as to remove inefficiencies from excessive manual handling and improve the quality of the finish. However, since installation of the new finishing line, the company has been troubled by two different defects in the surface finish, 'blistering' and 'blooming'. The expensive rework necessary when conditions are conducive to either of these defects renders the semi-automated finishing line a failure and the capital investment a waste.

The surface finish is said to *blister* when bubbles form under/in it. The bubbles are small, around one millimetre in diameter and occur in patches of about ten square centimetres in size. Sometimes it appears that the bubbles burst on the surface leaving small craters and sometimes they remain trapped under a smooth surface skin. A mixture of bubbles and craters is also possible. Blistering is more prevalent in hot weather but can occur all the year round. It is the most frequently observed defect in the surface finish. Both Nexus and the coatings supplier believed blistering to be a result of one or more of the coatings drying too quickly, an opinion that is supported by the fact that, when this problem is severe, the coatings supplier specifies an amount of 'retardant' to add to the lacquer coatings to slow the drying rate.

In cold or humid weather white milky patches may appear in the surface finish. This is known as *blooming*. These patches can be quite large, in excess of ten square centimetres in area. This is a much less frequently observed defect and,

¹Department of Applied Mathematics, University of Adelaide, SA 5005, Australia. Email ystokes@maths.adelaide.edu.au

²School of Pharmaceutical, Molecular and Biomedical Sciences, University of South Australia, Mawson Lakes SA 5095, Australia. Email Phillip.Pendleton@unisa.edu.au

apart from reworking the affected items or ceasing work until weather conditions improve, no corrective measures are currently taken when it is observed. Nexus believed this problem to be associated with very slow drying of the coatings.

Nexus came to the MISG wanting first and foremost to determine the exact causes of the two types of surface defect. Then, with this knowledge, they wanted to determine if the finishing line could be modified to prevent the problems and, if so, how. Already a large sum of money had been spent on the finishing line with little, if any, return, and they did not want a repeat of this experience. Furthermore, the daily product output of the factory had to be maintained and it was considered extremely desirable that suggested modifications to the finishing line be possible within the existing factory floor space and using the existing infrastructure.

2. The finishing process

A schematic diagram of the finishing process and factory layout, as seen during a visit to the factory in early January 2001, is given in Figure 1. The description of the process that follows is based on observations made during that visit and information supplied at that time and during the MISG week by the company representative.

Unfinished items of furniture from the stockpile area are loaded onto chip-board pallets and manually moved into the stain-spray booth which consists of an open area of the factory backed by a wall of filters; fans behind this wall draw air from the factory through the filters which should remove contaminants from the air and so clean it. Each item of furniture is sprayed with stain by hand, after which it is manually moved into the drying area, which is another spray booth. At the time of our visit to the factory, the filters at the back of the drying area were quite dark (probably clogged) adjacent to the stain-spray area, due to drift of stain during spraying. Despite the operation of the fans behind the spray booths, air movement in both spray and drying areas was imperceptible and stained furniture was being stacked in the drying area with little regard for encouraging air flow to aid quick drying.

Furniture is manually transferred on a first-come-first-served basis, from this drying area to yet another spray booth where the first (seal) lacquer coat is applied, again by hand spraying. The transfer rate varies depending on the time taken to apply the lacquer coat to individual items of furniture. There is no guarantee of a minimum length of stay in the drying area but it is thought that the lacquer is applied 7 to 10 minutes after staining.

After application of the first (acid cured) lacquer coat the furniture is manually transferred to a corner of the factory, known as the 'flash dry' area. Here

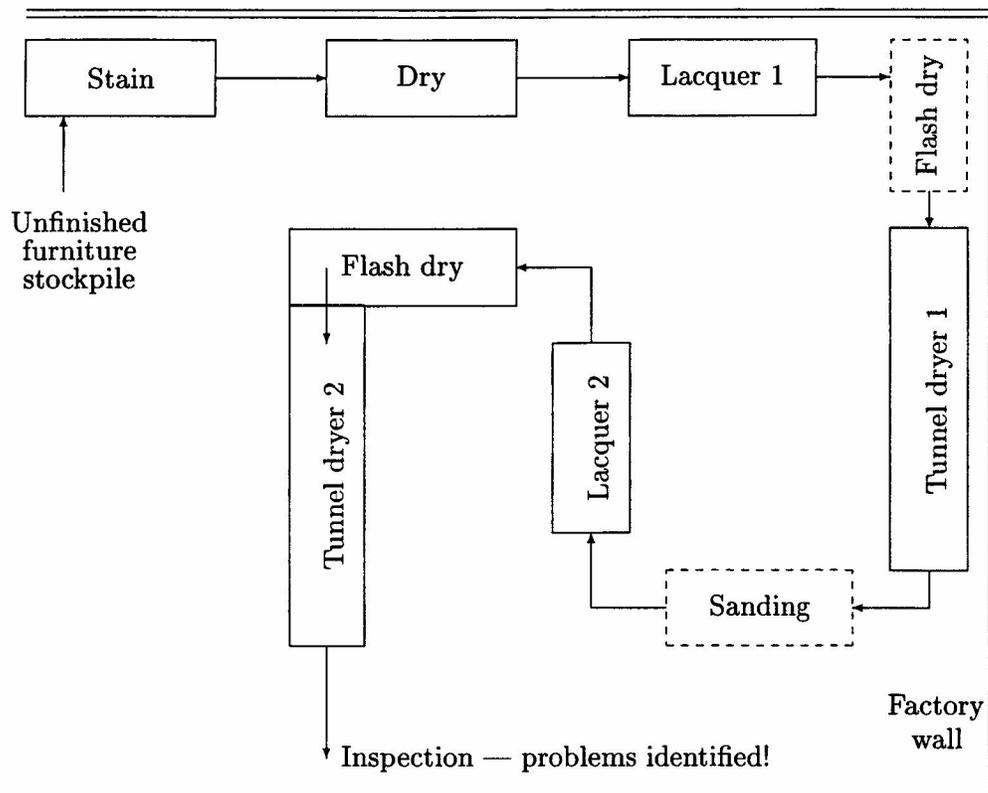


Figure 1: The Nexus finishing process.

the most volatile solvents should evaporate before the furniture enters the first drying tunnel. There is no assisted air movement in this area. The coatings manufacturer advises a 7 minute flash-off time at a temperature of 25°C, but in practice each item of furniture spends a maximum of 4 minutes at ambient air temperature (5–30°C depending on the time of year) in the flash dry area.

Furniture is next moved by hand into the first drying tunnel. This is a long tunnel, approximately 2 metres wide by 3 metres high by 10 metres long, open at each end, through which the furniture passes on an automated roller conveyor. Warm air is blown in through vents just above the level of the conveyor, and passes out through vents in the ceiling. Some of the air is vented to the outside atmosphere and some is recycled back into the drying tunnel. The amount of recycling is such that the solvent concentrations in the tunnel air are intended to be kept below the 'flash point' at which ignition could occur. According to the lacquer supplier the temperature profile in the tunnel and the speed of the conveyor should be such that an item of furniture experiences a temperature increase from 25°C to 40°C over a 7 minute period, a period of 7 minutes at a

constant temperature of 40°C, and a temperature decrease back to 25°C over a further 7 minutes, giving a total of 21 minutes in the tunnel. In fact, it takes about 14 minutes for an item of furniture to pass through the tunnel and the air temperature, at the probe position in the centre of the tunnel near the ceiling, while intended to be maintained at 45°C, may be as low as 18°C on a cold winter day due to insufficient capacity in the heat exchanger.

From the first drying tunnel, furniture is manually moved to the sanding area where it is given a light sand to prepare the surface for the final lacquer coat to give a semi-gloss finish. Blooming may be detected at this stage. After sanding the furniture is manually transported to a spray booth where the final lacquer coat is hand-sprayed.

As with the first lacquer coat the furniture is again moved to a flash dry area to allow evaporation of the most volatile solvents. However, this area is integrated with the second drying tunnel and hence is partially enclosed and has a few vents discharging warm air into it.

Next the furniture is transferred (manually) onto an automated roller conveyor which carries it through the second drying tunnel. This is constructed similarly to the first tunnel, but the air temperature is increased to a maximum of 35°C at the centre, the upper limit of the temperature range appropriate for curing of the (nitro-cellulose) second lacquer.

This completes the finishing process. After exiting the second tunnel dryer, the furniture is inspected before shipping. It is here that blooming or blistering of the surface finish is normally detected because these defects are more easily seen on the finished semi-gloss surface.

3. Preliminary analysis

A considerable amount of mathematical modelling has been done over many years on a variety of surface coating defects (see the discussion and reference list in [8]). In recent years attention has been given to surface levelling and film thickness variations due to the interaction of gravity and surface tension gradients (see, for example, [19, 7, 15]), but these are not matters of current concern to Nexus. Of seemingly more relevance is work on the formation of small craters due to flow driven by surface tension gradients, i.e. Marangoni effects, [6]. But the craters sometimes seen in furniture coatings at Nexus are due to bursting of bubbles, as is evident from the fact that patches of bubbles and craters, as well as just bubbles or just craters, may be seen.

The blistering defect is briefly discussed in Turner [14, p. 130], where it is termed *popping*. The usual causes are given as:

1. inadequate drying at room temperature before the paint is stoved (i.e. cured in an oven);
2. the presence of too much low (or medium) boiling solvent;
3. reaction in the paint producing a gas; or
4. a faulty or contaminated undercoat.

We immediately note the first of these as a prime suspect, corresponding to too little time in a flash-dry area.

Blooming, which occurs much less frequently than blistering and only in cold or humid weather, can be expected to have a different cause. This defect is also briefly discussed in Turner [14], where it is termed *blushing*. Two possible causes are indicated:

1. incompatible transparent resins which dry to give a milky film [14, p. 75];
and
2. condensation on a clear film and subsequent emulsification of water in the film; evaporation of the water after the film has set leaves fine air bubbles in the film [14, p. 130].

Both of these are plausible in cold or humid conditions and are consistent with the fact that blooming may be detected after application and drying of the first lacquer coat and before application of the second. Slow drying conditions may result in a (lacquer) coating being applied over a previous (stain or lacquer) coating that is not sufficiently dry, and a possible mixing of incompatible resins. Probably even more likely is the formation of condensation on a wet coating surface or on furniture waiting for the finishing coatings to be applied. It is conceivable that, on a cold winter morning when the factory temperature can be as low as 2–8°C, the moisture in a sprayer's breath may condense on the furniture he is spraying.

For several reasons it was agreed during the MISG week that efforts should be focussed on determining the cause of and possible remedies for blistering. Firstly, this is the most prevalent of the two types of observed defect and most savings will be made by rectifying this problem. Secondly, the problem seemed to be associated with the drying process which was identified as conducive to

mathematical analysis, while blooming was seen as a more chemical problem requiring experiments and chemical analysis that would be better undertaken by the company after the MISG week.

4. Bubble sources

Blistering is clearly associated with the formation of bubbles in a coating. As described in [8], there are a variety of possible reasons for bubbles appearing in the types of sprayed coatings used by Nexus.

1. In airless spraying systems, as used by Nexus for application of lacquer coatings, high pumping pressures are used. Under these conditions air solubility is higher than at atmospheric pressure and air contained in any air bubbles in the coating mixture will dissolve in the coating solutions. When the pressure returns to atmospheric pressure as the coating exits the spray nozzle and deposits on the furniture, this air comes out of solution and may form bubbles in the coating film.
2. There may be entrainment of air during spraying, although the method in use is one that should minimise this so this does not seem a likely cause of bubbles.
3. Dirt on the substrate may give rise to bubbles underneath the coating which cannot stick to the substrate.
4. Air in the pores of the substrate, if pressed out into the paint film due to wetting conditions or heating, may give rise to bubbles.
5. The impact of spray drops on a wet substrate may cause bubbles, due to splashing.
6. When a coating is heated to aid drying, volatiles in the coating may boil and form bubbles in the coating film.
7. Gaseous reaction between the different coatings, if a coating is applied before the previous one has dried sufficiently, may also be a source of bubbles.

Of these, item 6 was first considered as a very plausible explanation of blistering at the Nexus factory which called for a detailed investigation. Specifically it was thought that the usual too short a time in the flash-off area prior to entering the first drying tunnel could result in highly volatile solvents remaining in the coating, entering the tunnel and there boiling. Over the complete finishing

process, the air temperature reaches a maximum (of around 45°C in sufficiently warm weather) midway along the first drying tunnel, so that this seemed the most likely location for solvent boiling to occur.

5. The classic drying profile, ‘skinning’ and bubble-point

The drying of thin films is a topic of very active current research in a variety of industrial contexts such as automotive paint shops, ink-jet printing, adhesives and magnetic media [1, 9, 10, 12, 16, 17, 18]. It has also been considered in an environmental context where there is concern about the emissions of organic compounds from coatings over a long time period [20]. Of particular relevance, Price and Cairncross [12] have considered bubbling due to solvent boil during heat-assisted drying and how to optimize oven conditions for maximum drying speed without solvent boil.

In that paper [12] the classic drying profile (in a drying oven) is described as consisting of three distinct stages.

1. **The warm-up period** during which the film temperature increases rapidly till the rate of energy supplied nearly equals the energy consumption due to evaporation of solvents.
2. **The constant-rate period** during which the film surface remains wet and the drying rate remains practically constant with the rate of solvent diffusion to the surface equal to the rate of evaporation from the surface. The supplied energy is totally consumed in effecting a phase change of the solvents and not in any temperature increase.
3. **The falling-rate period** during which the evaporation rate drops so that the heat energy supplied is no longer being totally consumed in the evaporation process. Then the film temperature rises to the oven temperature. The evaporation rate drops either because the coating layer runs out of solvent or because the rate of diffusion of solvents to the surface slows below the evaporation rate so the surface dries out while the bulk coating layer remains wet — known as *diffusion-controlled drying*.

Ideally, the oven temperature profile and the solvent concentration in the oven air and the air flow, which are the controls to the drying process, are such that there is a sufficiently long constant-rate period during which all of the solvents are removed from the coating film, and the falling-rate period is entered because of a lack of solvents in the coating. However, oven conditions must be very finely tuned for the specific coatings in use to achieve such an ideal.

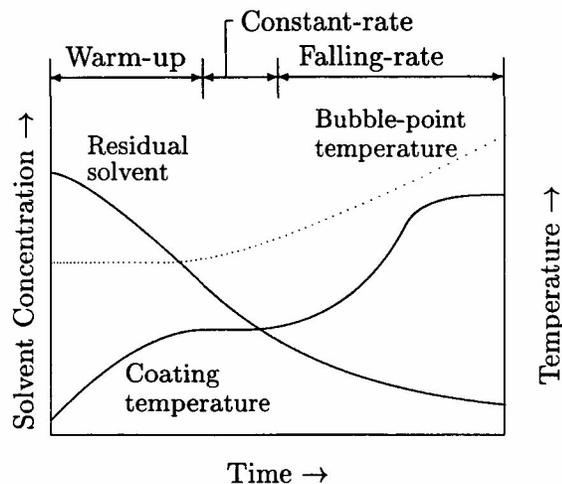


Figure 2: The classic drying profile.

Rather diffusion-controlled drying is normal in a polymer-solvent system, where the diffusion coefficient is strongly concentration dependent and may decrease by several orders of magnitude as the solvent concentration decreases and the polymer concentration increases [12]. This leads to a phenomenon known as *skinning* where there is a strong solvent concentration gradient, from high concentration at the substrate-film interface to near-zero at the film-air interface. Polymerization at the film-air interface to form a semi-impermeable barrier which greatly reduces the rate of solvent diffusion to the surface will enhance the skinning phenomenon.

The rise in film temperature that accompanies the falling-rate period may lead to the boiling of solvents trapped in the film below the surface skin. This will occur if the local film temperature at any position within the film exceeds the *bubble-point temperature*, defined to be 'the temperature at which the local equilibrium solvent partial pressure (as computed at a hypothetical internal interface) equals ambient pressure' ([12]). Then bubbles form in the coating film at this position and, if they remain trapped below the surface skin, they are seen as a defect in the coating. If they do rise to and burst at the film surface, and the surface is not sufficiently fluid to level, then craters will be seen instead of bubbles. This is consistent with the bubbling problem experienced by Nexus.

The classic drying profile is illustrated in Figure 2 in terms of the residual solvent concentration and the coating film temperature. The minimum bubble-point temperature curve is also shown (dotted), obtained by finding the lowest bubble-point temperature within the whole film; the bubble-point temperature for a single solvent begins at the boiling point of the solvent and increases as

the solvent concentration decreases. For a mixture of solvents the bubble-point temperature will vary as the more volatile components evaporate and the mixture content changes. In Figure 2, the bubble-point temperature is always higher than the coating temperature so no bubbles form.

6. Formation and growth of vapour bubbles

The data sheets provided by Nexus for the stain and lacquer coatings used give boiling point data as follows.

Coating	Boiling Point (°C)
Stain	78–199
Lacquers	78–174

Presumably the ranges cover the boiling points of all the different constituents that make up the solvent mixtures, not all of which are specified on the data sheets. Ethanol seems to be the component of lowest boiling point (78°C) used in the three coatings. Hence, we expect the initial bubble-point temperature for each of the coatings to be 78°C or higher, and to rise as the more volatile solvents, such as ethanol, evaporate.

Having determined this, we see immediately that, even if skinning does trap solvent in the coating, boiling of solvent only cannot account for blistering in the Nexus finishing process. After all, the maximum temperature reached in the finishing line is 45°C in the first drying tunnel, well below the minimum bubble-point temperature for any of the solvent mixtures in use. Hence other factors must be considered to explain the formation of bubbles.

One possibility that was considered during the MISG week was air bubbles nucleating from pores in the substrate. Another is dissolution of dissolved gases with which a coating solution may become supersaturated during processing [4, 8]. To understand both of these mechanisms we need to consider the formation and growth of vapour bubbles in a heated liquid. The discussion below is derived from that in Baehr and Stephan [2, pp. 448–451].

For a gaseous bubble of radius r to be in static equilibrium in a pure liquid, surface tension forces must balance net pressure forces. The bubble will contain vapourised liquid at saturation pressure p_{sat} and, perhaps, other gases (e.g. air) also. Let p_g be the sum of the partial pressures of all the other gases present. Then, with surface tension σ and ambient pressure in the surrounding liquid p_ℓ , we must have

$$2\pi r\sigma = (p_{sat} + p_g - p_\ell)\pi r^2 \quad \text{or} \quad p_{sat} + p_g = p_\ell + \frac{2\sigma}{r}. \quad (1)$$

We note that at a perfectly flat interface ($r = \infty$) with $p_g = 0$ we have $p_{sat} = p_\ell$, i.e. the saturation vapour pressure of the liquid must equal the ambient liquid pressure, which is approximately equal to atmospheric pressure. This is attained at the boiling point of the liquid [11, p. 267] and is consistent with the definition of bubble-point temperature above. However, for a spherical vapour bubble with $p_g = 0$, the saturation vapour pressure must exceed p_ℓ by an amount $2\sigma/r$, i.e. the liquid around the bubble must be ‘superheated’ above the boiling point temperature to achieve a saturation vapour pressure in excess of atmospheric pressure. On the other hand, if the bubble contains gases in addition to the vapourised liquid so that $p_g > 2\sigma/r$ then it will be in static equilibrium at a temperature *below* the boiling point temperature of the liquid. At a given temperature there is a critical bubble size $r = r^*$ that is in equilibrium with the liquid. Smaller bubbles will collapse while larger bubbles will grow.

Now, even a liquid with good wetting ability cannot completely fill the very small cavities in a surface which it covers. These will contain vapourised liquid and other gases that will expand with heating. These vapour and gas pockets will form viable bubbles attached to the surface if they expand to the critical bubble size as defined above. If superheated above the temperature necessary to maintain the critical size, a bubble will grow until it develops sufficient buoyancy to detach from the surface.

Without more precise information on where blistering is occurring in the Nexus finishing process it is difficult to determine exactly what, if any, application the above theory may have. Application is complicated by the fact that we are not dealing with a pure liquid but with polymers and other solids dissolved in a mixture of solvents. Not all of the constituents are known and, for those that are, precise quantities are unknown. Both during the MISG week and after, considerable effort was put into estimating saturation pressures for each of the coatings, assuming that each component in a solvent mixture behaves as a pure solvent. In the end, however, the calculations were so simplified that the results could not be used with any degree of confidence and we have rather used data from [13] to estimate solvent properties. Most of the time the solvent mixture in each coating solution is treated as a pure ideal liquid with the properties of ethanol, one of the most volatile of the solvent constituents and hence that most likely to cause blistering. With this explanation, we suggest the following scenario as a plausible mechanism for blistering.

Very volatile solvents such as ethanol in the stain and first lacquer coatings applied to a timber item may not have sufficient time to evaporate in the short time spent in the first flash dry area. On entering the first drying tunnel the rise in temperature results in dissolved gases in the coatings coming out of solution and expansion of the gases in the pores in the timber substrate, as well as

skinning of the lacquer coating. Vaporisation of very volatile solvents adds to the gas pressure in the forming bubbles.

We have estimated surface tension and saturation vapour pressure data from data in [13] as follows. Using the general nomograph on p. 610 we determined the surface tension at 40°C of the known solvents in the coating solutions (ethanol, n-butanol, toluene, xylene, methyl ethyl ketone) and took an upper limit of about 27 dyn/cm (for xylene). Vapour pressure has been calculated from the Antoine equation (p. 629) with coefficients as given for ethanol (p. 638), yielding a value of 133 mm Hg or $0.175p_a$, where $p_a = 760 \text{ mm Hg} = 1.01325 \times 10^6 \text{ dyn cm}^{-2}$ is atmospheric pressure.

Now, with $p_\ell = p_a$ we obtain the following relationship between critical bubble radius (in mm) and gas partial pressure p_g :

$$\frac{p_g}{p_a} = \frac{0.00533}{r^*} + 0.825.$$

Then, for $r^* = 0.1 \text{ mm}$ a gas partial pressure of 0.878 atmospheres is required, which seems quite possible. As the temperature rises higher, up to around 45°C, these bubbles will become superheated and grow, perhaps to the observed size of around 0.5 mm in radius. As their buoyancy increases with size, they will rise towards the surface. If skinning is not too advanced they may burst at the surface; otherwise they will be trapped below the surface skin. In warm weather when the ambient air temperature in the factory is relatively high, the formation and growth of bubbles may begin in the flash dry area prior to entering the drying tunnel.

This scenario is consistent with the literature that indicates that blistering is associated with too short a drying time at room temperature [8, 14]. It is also consistent with Nexus experience that blistering may occur all year round but is most common during warm weather. Of course, other scenarios are also possible.

7. A mathematical skinning model

Whatever the mechanism by which bubbles are formed in a coating, skinning would appear to be the critical factor that prevents or impedes their escape, resulting in a visible defect. Hence, a mathematical model of film drying in a heated tunnel has been developed so as to determine the conditions under which skinning becomes a serious problem.

Equations to model the drying of thin films on an impermeable substrate are given in [12], but these are more complex than is thought necessary or justifiable

for the present problem, especially considering the serious lack of data on the various coatings used by Nexus (see later). Hence, these have been modified by making a number of additional simplifying assumptions to yield a model which is believed to be a useful starting point in giving a feel for the drying process and the important parameters involved.

Although a porous timber substrate is definitely not impermeable to the coating solvents, this is a valid approximation if, as we expect, evaporation of solvents through the coating-air interface is much more rapid than permeation of solvent into the timber. In addition we have

- ignored shrinkage of the coating film as it dries because, even though solvents initially constitute some 60% or more of the total coating mass, bubbling brought about by skinning is most likely when the bulk coating is still quite wet;
- assumed the diffusion coefficient of the solvent mixture to be constant in both space and time, even though it is strongly dependent on solvent concentration;
- assumed the solvent mass-transfer coefficient to be a constant parameter although it will depend on both temperature and air velocity;
- for reasons given earlier, treated a coating as a binary system comprised of a polymer and a pure solvent with the properties of ethanol.

Because the surface area covered by the coating is large compared with its thickness L a one-dimensional model is suitable. Any curvature of the substrate may also be ignored on the basis that it is large compared with the coating thickness. Thus we have considered the drying of a thin coating on a flat impermeable substrate. We set the origin at the substrate-film interface with the x -axis directed through the coating, as shown in Figure 3. Equations governing both solvent concentration $c(x, t)$ and temperature $\theta(x, t)$, as functions of height x above the substrate and time t , are required.

7.1 Solvent concentration

Transport of solvent within the coating film is (at least primarily) by diffusion so that we must solve the diffusion equation for $c(x, t)$ over the region $0 \leq x \leq L$ which, assuming a constant diffusion coefficient D is

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \quad (2)$$

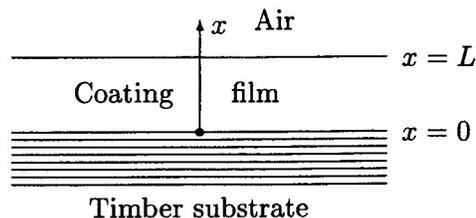


Figure 3: Model problem.

At the substrate-film interface $x = 0$ we apply a zero-flux boundary condition

$$\frac{\partial c}{\partial x}(0, t) = 0. \quad (3)$$

Evaporation of solvent from the film-air interface is dependent on the difference between solvent partial pressure at the film surface p_S and that in the bulk air p_A [2, 12]. Hence, by analogy with Newton's law of cooling we have

$$-D \frac{\partial c}{\partial x}(L, t) = k_c(p_S - p_A), \quad (4)$$

where k_c is the mass transfer coefficient (assumed constant). Since $p_A \ll p_S$ it is reasonable to take $p_A \approx 0$ and further simplify this boundary condition.

As described in [12, 13], a value for p_S may be computed from the saturation pressure for ethanol p_{sat} and the Flory-Huggins equation for solvent activity thus:

$$p_S = p_{sat} \phi_S f(\phi_P), \quad f(\phi_P) = \exp(\phi_P + \chi \phi_P^2), \quad (5)$$

where ϕ_S , ϕ_P are the volume fractions of solvent and polymer at the film-air interface and χ is the Flory-Huggins interaction parameter. The volume fractions are given by the solvent concentration: $\phi_S = c(L, t)/\rho_S$, $\phi_P = 1 - \phi_S$, where ρ_S is the density of the solvent so that the boundary condition at $x = L$ may be written

$$-D \frac{\partial c}{\partial x}(L, t) = \frac{k_c p_{sat}}{\rho_S} c(L, t) f(\phi_S) \quad (6)$$

where

$$f(\phi_S) = \exp(1 - \phi_S + \chi(1 - \phi_S)^2).$$

For $\chi = 0.39$ (see [12]), $f(\phi_S)$ increases from 1 to 4 as ϕ_S decreases from 1 to 0.

The initial concentration of solvent throughout the coating thickness is constant, i.e. $c(x, 0) = c_0$.

Defining dimensionless variables

$$c = c_0 C, \quad x = LX, \quad t = \frac{L^2}{D} T \quad (7)$$

we obtain

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial X^2}, \quad 0 \leq X \leq 1, \quad (8)$$

with boundary conditions

$$\frac{\partial C}{\partial X}(0, T) = 0, \quad (9)$$

$$-\frac{\partial C}{\partial X}(1, T) = \alpha C(1, T) f(\phi_S), \quad \alpha = \frac{k_c L p_{sat}}{D \rho_S}, \quad \phi_S = \frac{c_0}{\rho_S} C(L, t), \quad (10)$$

and initial condition

$$C(x, 0) = 1. \quad (11)$$

7.2 Thermal model

Heat transfer within the coating is also by diffusion so that temperature $\theta(x, t)$ over $0 \leq x \leq L$, measured in Kelvin, is given by

$$\rho C_p \frac{\partial \theta}{\partial t} = k_\theta \frac{\partial^2 \theta}{\partial x^2}, \quad (12)$$

where ρ is density (of the coating solution as a whole), C_p is specific heat and k_θ is the thermal conductivity. The boundary conditions are

$$\frac{\partial \theta}{\partial x}(0, t) = 0, \quad (13)$$

assuming the substrate-film interface to be a perfectly insulated boundary, and

$$-k_\theta \frac{\partial \theta}{\partial x}(L, t) = h(\theta(L, t) - \theta_a) + \frac{\lambda k_c p_{sat}}{\rho_S} c(L, t) f(\phi_S), \quad (14)$$

where loss of heat energy through the coating-air interface is equal to heat conduction through $x = L$ (given by Newton's law of cooling) plus the latent heat consumed in the evaporation of solvent. h is the heat-transfer coefficient, θ_a the air temperature and λ the latent heat of vaporisation for the solvent. The initial temperature throughout the coating is constant at $\theta(x, 0) = \theta_0$.

Note that the air temperature in a drying tunnel varies along its length so that, for a coating moving through the drying tunnel, the air temperature is some prescribed function of time. At this stage, however, we have assumed a constant air temperature θ_a although this can be readily changed.

Again we non-dimensionalize using (7) and

$$\theta = \theta_a(1 + \Theta) \quad (15)$$

to give

$$\frac{\partial \Theta}{\partial T} = \beta \frac{\partial^2 \Theta}{\partial X^2}, \quad 0 \leq X \leq 1, \quad \beta = \frac{k_\theta}{\rho DC_p} \quad (16)$$

with boundary conditions

$$\frac{\partial \Theta}{\partial X}(0, T) = 0 \quad (17)$$

and

$$-\frac{\partial \Theta}{\partial X}(1, T) = \gamma (\Theta(1, T) + \delta C(1, T) f(\phi_S)), \quad (18)$$

where

$$\gamma = \frac{Lh}{k_\theta} \quad \text{and} \quad \delta = \frac{\lambda k_c p_{sat} c_0}{h \theta_a \rho_S}.$$

The initial condition is just

$$\Theta(x, 0) = \frac{\theta_0 - \theta_a}{\theta_a}. \quad (19)$$

8. Solvent properties

To determine suitable values for each of the model parameters we require considerable information on the coating mixtures, much of which is lacking. Specifically we have five dimensionless parameters

$$\begin{aligned} \alpha &= \frac{k_c L p_{sat}}{D \rho_S}, & \beta &= \frac{k_\theta}{\rho DC_p}, & \gamma &= \frac{Lh}{k_\theta}, \\ \delta &= \frac{\lambda k_c p_{sat} c_0}{h \theta_a \rho_S}, & \mu &= \frac{c_0}{\rho_S}, \end{aligned} \quad (20)$$

defined in terms of twelve physical constants, along with the Flory-Huggins interaction parameter. To obtain (hopefully) reasonable estimates for these parameters data has been gathered from a variety of sources, assuming the solvent to be ethanol. The c.g.s. system of units has been adopted.

We take $\theta_a = 313 \text{ K}$ and $L \approx 10^{-4} \text{ cm}$ and, from [13], we have $\rho_S = 0.78 \text{ g cm}^{-3}$ and (see earlier) $p_{sat} = 1.77 \times 10^5 \text{ dyn cm}^{-2}$. We also, initially, use the data in Table 1 derived from [12] for a coating with polyvinyl acetate as the solid component and toluene as the solvent. Toluene is one component of the Nexus coatings. Albeit, it should be noted that the temperature regime considered in [12] is much higher than what pertains in the Nexus finishing process.

Table 1: Assumed properties of the coating mixture.

ρ	(g cm ⁻³)	1.0
C_p	(cal g ⁻¹ K ⁻¹)	0.4
k_θ	(cal cm ⁻¹ s ⁻¹ K ⁻¹)	3.5×10^{-4}
λ	(cal g ⁻¹)	100.0
D	(cm ² s ⁻¹)	4.0×10^{-4}
c_0	(g cm ⁻³)	0.65
χ		0.39

Table 2: Properties for the Chilton-Coburn analogy.

M	(g)	46.1	[13, p. 636]
ρ_a	(g cm ⁻³)	1.127×10^{-3}	[3, Appendix 1]
C_{p_a}	(cal g ⁻¹ K ⁻¹)	0.26	[5, pp. 438–9]
κ_a	(cal cm ⁻¹ s ⁻¹ K ⁻¹)	6.4×10^{-5}	[3, Appendix 1]
D_a	(cm ² s ⁻¹)	0.145	[13, p. 557]
R	(erg K ⁻¹ mol ⁻¹)	8.314×10^7	[11, p. 278]

The mass transfer coefficient k_c (s cm⁻¹) can be derived from the heat transfer coefficient h (cal cm⁻² s⁻¹ K⁻¹) using the Chilton-Coburn analogy [12]

$$\frac{hM}{k_c} = \rho_a C_{p_a} R \bar{\theta} \left(\frac{\rho_a C_{p_a} D_a}{\kappa_a} \right)^{-0.67},$$

where ρ_a , C_{p_a} and κ_a are the density, specific heat and thermal conductivity of air at the temperature $\bar{\theta}$, which is the average of the temperatures at the film-air interface and in the bulk air. Although $\bar{\theta}$ varies in time we assume a constant value of 40°C = 313 K. D_a is the diffusivity of the solvent in air also at temperature $\bar{\theta}$ and M is the molecular weight of the solvent (i.e. ethanol). The data used are given in Table 2 along with references.

Putting this all together we obtain

$$\begin{aligned} \frac{h}{k_c} &\approx 2 \times 10^5, & \alpha &= \frac{k_c L p_{sat}}{D \rho_S} \approx 0.3 h, & \beta &= \frac{k_\theta}{\rho D C_p} \approx 2, \\ \gamma &= \frac{Lh}{k_\theta} \approx 0.3 h, & \delta &= \frac{\lambda k_c p_{sat} c_0}{h \theta_a \rho_S} \approx 0.2, & \mu &= \frac{c_0}{\rho_S} = 0.83. \end{aligned} \quad (21)$$

The heat transfer coefficient h varies with temperature and air velocity and, with reference to [12], we consider $h = 10^{-4}$ cal cm⁻² s⁻¹ K⁻¹.

9. Solving the equations

The model defined above is readily solved by an explicit forward-time centred-space (FTCS) finite-difference scheme. For this we define a grid of N equally spaced nodes over $0 \leq X \leq 1$, $X_j = (j - 1)\Delta X$, $j = 1, \dots, N$ with $\Delta X = 1/(N - 1)$, and a time step ΔT .

Then, with respect to the solvent concentration model, (8) becomes

$$C_j^{n+1} = C_j^n + s \left(C_{j+1}^n - 2C_j^n + C_{j-1}^n \right), \quad j = 2, \dots, N - 1, \quad n = 0, 1, \dots, \quad (22)$$

where $s = \Delta T/(\Delta X)^2$ and C_j^n is the solvent concentration at the j -th node and n -th time step. At $j = 1$ (i.e. on the boundary $X = 0$) we have, using (9),

$$C_1^{n+1} = C_1^n + 2s(C_2^n - C_1^n), \quad n = 0, 1, \dots \quad (23)$$

and at $j = N$ (i.e. on the boundary $X = 1$) we have, using (10),

$$C_N^{n+1} = C_N^n + 2s \left(C_{N-1}^n - (1 + \alpha\Delta X f(\mu C_N^n)) C_N^n \right), \quad n = 0, 1, \dots \quad (24)$$

With respect to the thermal model, (16) becomes

$$\Theta_j^{n+1} = \Theta_j^n + \beta s \left(\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n \right), \quad j = 2, \dots, N - 1, \quad n = 0, 1, \dots, \quad (25)$$

where Θ_j^n is the temperature at the j -th node and n -th time step, while at $j = 1$ we have, using (17),

$$\Theta_1^{n+1} = \Theta_1^n + 2\beta s(\Theta_2^n - \Theta_1^n), \quad n = 0, 1, \dots \quad (26)$$

and at $j = N$ we use (18) to obtain

$$\Theta_N^{n+1} = \Theta_N^n + 2\beta s \left(\Theta_{N-1}^n - (1 + \gamma\Delta X)\Theta_N^n - \gamma\delta\Delta X f(\mu C_N^{n+1})C_N^{n+1} \right), \quad n = 0, 1, \dots \quad (27)$$

Given $C_j^0 = 1$ and $\Theta_j^0 = (\theta_0 - \theta_a)/\theta_a$, $j = 1, \dots, N$, we solve first for solvent concentration then for temperature at each of the grid points at successive time steps to give concentration and temperature as functions of position in the coating film and time. For stability of the finite difference method we must choose ΔX and ΔT such that $s < 1/2$ (for computing concentration) and $s\beta < 1/2$ (for computing temperature). With $\beta = 2$ the second condition controls. We let $\Delta X = 0.1$ and $\Delta T = 0.001$, giving $s\beta = 0.2$.

Now, from our knowledge of the Nexus finishing process, evaporation is expected to occur over seconds or even minutes. Noting that the time scale is

$L^2/D = 2.5 \times 10^{-5}$ s, each time step of size $\Delta T = 0.001$ represents a physical time of 2.5×10^{-8} s. Hence, while our solution algorithm is quite straight forward, the explicit finite difference method used demands a very large number of time steps 4×10^7 for every second of physical time. This makes the computations fairly time-consuming but, otherwise, the solution method appears to work well.

10. Results

Solvent concentration profiles through the coating are shown in Figure 4, at time intervals of 0.1 seconds. The computations were made using parameter values as given above and the initial temperature in the coating was set at $20^\circ\text{C} = 293\text{ K}$, i.e. a dimensionless temperature of -0.064 . There is no evidence of skinning, with the solvent concentration being close to uniform throughout the coating thickness at any point in time. This indicates that for the parameter values chosen, the rate of diffusion is sufficiently fast to keep up with evaporation of solvents. Note also that evaporation occurs very quickly with solvent concentration being close to zero after just 1.4 seconds. This seems rather too fast compared with reality and suggests inaccuracies in assumed solvent properties and model assumptions, which is hardly surprising. The temperature throughout the coating thickness at any point in time is also quite uniform. Figure 5 shows coating temperature as a function of time. Note the evaporative cooling that occurs at early time, before evaporation slows and heating causes a rise in the coating temperature.

Now, we know that, in general, diffusivity decreases with temperature [13] so that our diffusion coefficient, based on the much higher temperatures in [12], is probably too large. Furthermore as solvent concentration decreases and polymerization of the coating takes place, diffusivity may decrease by orders of magnitude. Therefore, we look at the effect of reducing the value of the diffusion coefficient D . Reducing D by m orders of magnitude increases α and β and the time scale L^2/D by m orders of magnitude. Then, for stability of the finite difference computations we must reduce the time step by m orders of magnitude keeping $s\beta = 0.2$.

In Figure 6 we see the effect on solvent concentration of reducing the diffusivity by three orders of magnitude to $D = 4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. There is some evidence of skinning with the solvent concentration decreasing slowly from the substrate surface ($x/L = 0$) to the film-air interface ($x/L = 1$). Again the solvent concentration has nearly reached zero after 1.4 seconds. At any instant in time the temperature is close to constant through the coating thickness and the change in coating temperature with time, as shown in Figure 7, is quite similar to that seen previously.

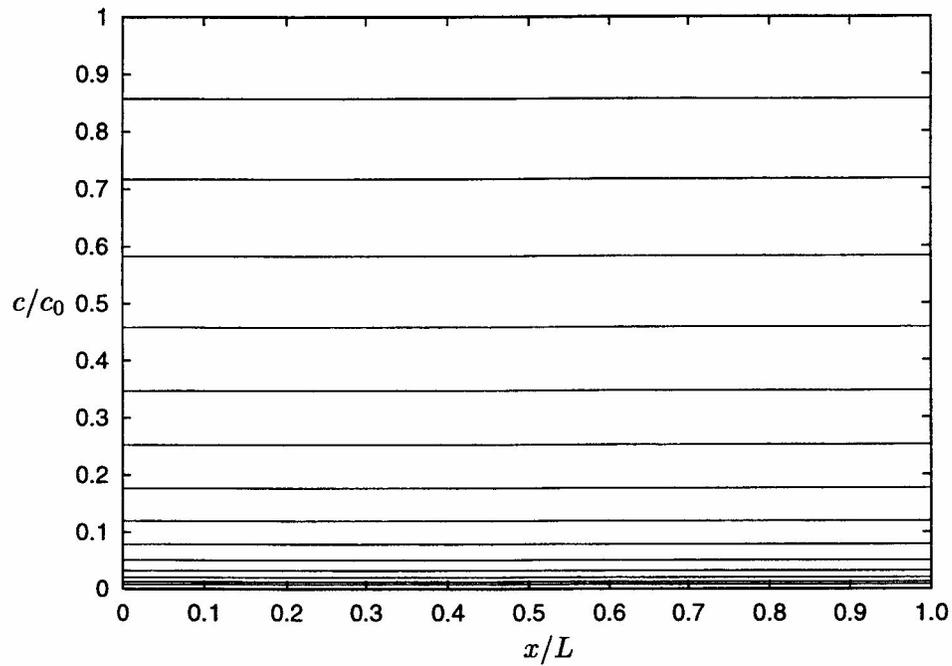


Figure 4: Solvent concentration c profiles through the coating at time intervals of 0.1 s, $0 \leq t \leq 1.4$ s, $D = 4 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$. Concentration decreases with time and there is no sign of skinning.

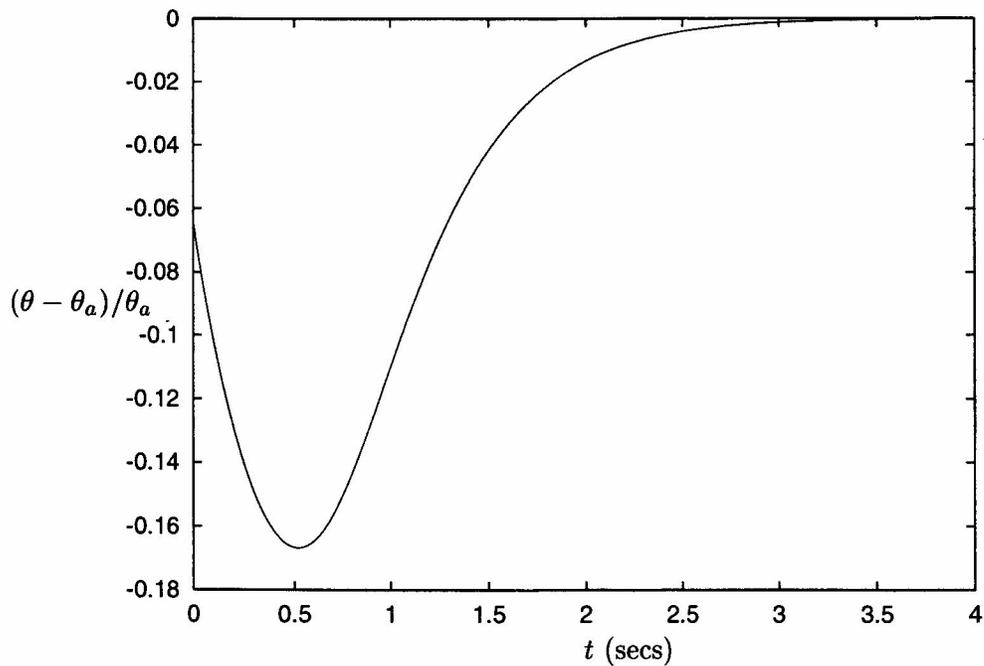


Figure 5: Temperature θ in the coating versus time t .

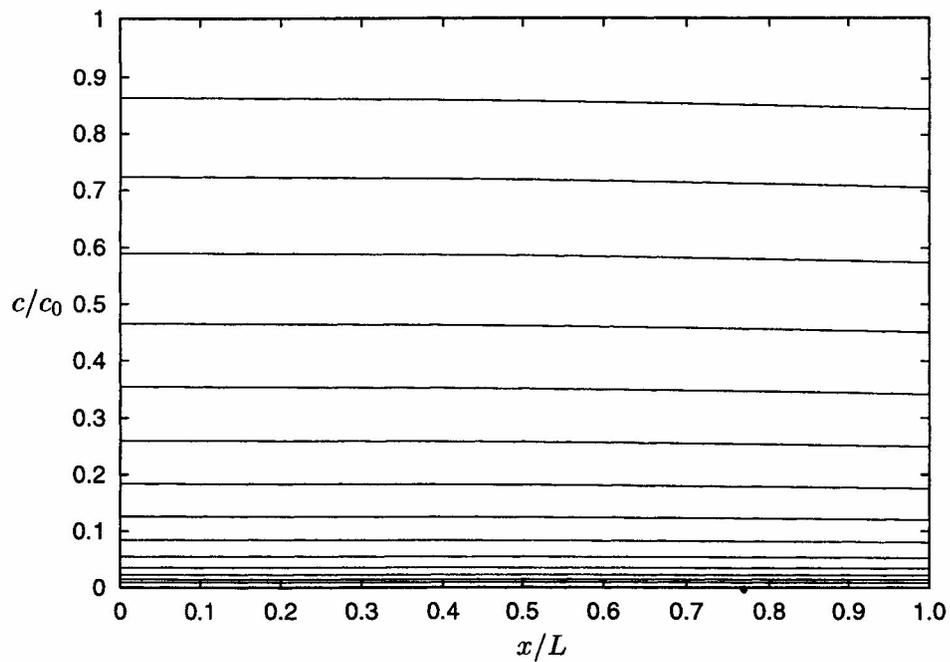


Figure 6: Solvent concentration c profiles through the coating at time intervals of 0.1 s, $0 \leq t \leq 1.4$ s, $D = 4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Concentration decreases with time and there is some sign of skinning.

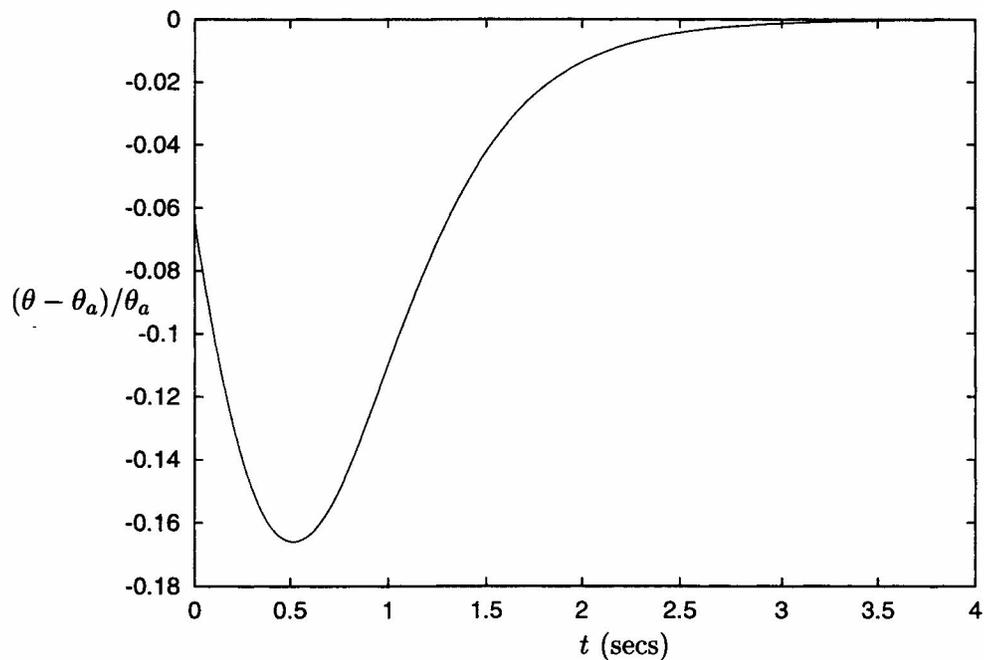


Figure 7: Temperature θ in the coating versus time t .

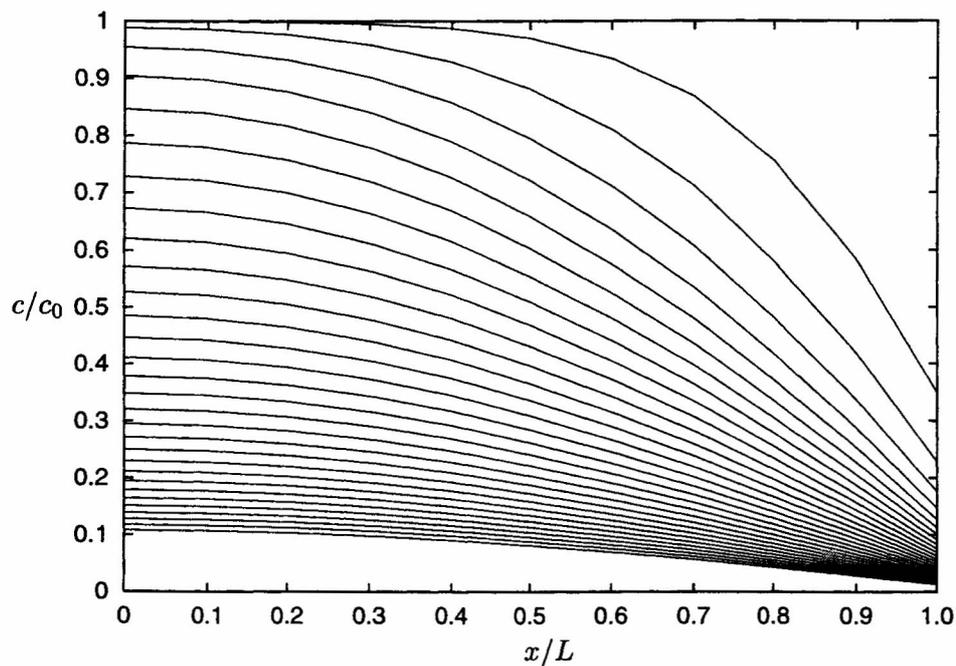


Figure 8: Solvent concentration c profiles through the coating at time intervals of 0.1 s, $0 \leq t \leq 3$ s, $D = 4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Concentration decreases with time and there is obvious skinning.

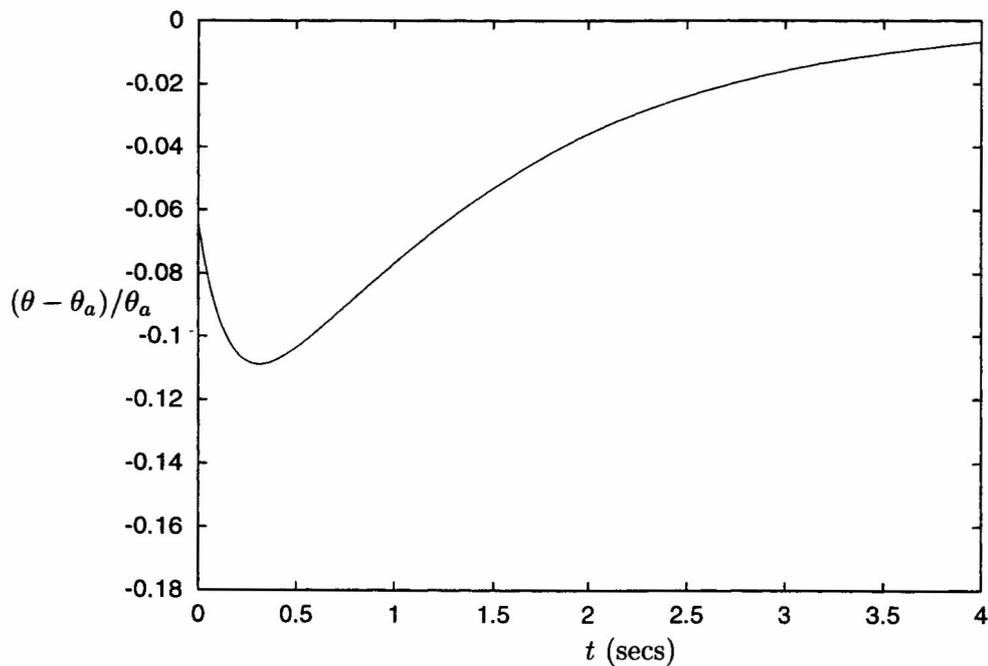


Figure 9: Temperature θ in the coating versus time t .

Reducing the diffusivity by another 2 orders of magnitude to $D = 4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, we obtain the results shown in Figures 8 and 9. Now there is obvious skinning of the coating seen as a pronounced decrease in solvent concentration from the substrate surface ($x/L = 0$) to the film-air interface ($x/L = 1$). Furthermore, the rate at which the solvent concentration in the coating decreases to zero is greatly reduced. After 3 seconds the solvent concentration at the substrate surface is still 10% of the initial value. Still the temperature is close to constant through the coating thickness at any instant in time but there is less of a temperature drop due to evaporative cooling and the temperature does not reach the ambient air temperature after 4 seconds. Overall, this behaviour is more as we expected and indicates that a better knowledge of diffusivity in the coatings used by Nexus, along with other properties, is necessary. Modifying the model to include the variation of the diffusion coefficient with change in solvent concentration and polymerization of the coating is essential to determining whether skinning is the cause of blistering in the Nexus finishing process but, at the present time, the available information does not permit this.

11. Conclusions and recommendations

Mechanisms for both the blooming and blistering defects of concern to Nexus have been suggested, but much more work is needed to establish the exact causes of these problems.

With respect to blooming, condensation of moisture on a wet coating, or on the substrate just prior to coating, is a possible cause. This could be investigated experimentally by spraying a mist of water on a wet coating and/or on the substrate just before applying a coating. This probably needs to be done under conditions in which the water does not evaporate too quickly, so simulating condensation on a humid or cold day. The result of applying a lacquer to a wet stain coating could also be investigated experimentally, to see whether there is any incompatibility between the two coating mixtures that might result in a blooming defect.

Attention was focussed on blistering which causes Nexus most trouble. We are reasonably certain that boiling of solvents is not the cause since operating temperatures are well below solvent boiling points. Rather, the likely sources of bubbles are dissolution of dissolved gases in a heated coating or nucleation of gas bubbles from pores in the timber substrate. The presence/absence of dissolved gases should be ascertained by testing of the coating solutions.

It is probable that skinning impedes the rise of bubbles to the coating-air interface where they burst leaving craters, or prevents them reaching the coating-

air interface at all so that they remain trapped in the coating. Skinning is due to rapid evaporative drying relative to the rate of diffusion to the coating-air interface. Thus, the coatings supplier and Nexus are probably correct in identifying the cause of blistering as too rapid drying, though not because of solvent boil as also thought.

Mathematical modelling of the drying process did not show conclusively whether skinning does or does not occur in the Nexus finishing process, although it was seen to be a definite possibility. The present model needs modification to remove a number of unrealistic assumptions (e.g. a constant diffusivity) that have a strong impact on the results. Even more importantly and to enable the development of a more realistic model much more information is needed on the coatings and their properties. Careful monitoring of the finishing process and identification of the stage(s) when blisters are formed would also be of considerable benefit.

From the work done to date we do suspect that both blistering and blooming problems could be alleviated by enlarging the first flash-dry area so that more time is spent, after application of the first lacquer, drying at room temperature before heating in the first drying tunnel. This may enable evaporation of any condensation and of more of the volatile solvents, as well as escape of any gases coming out of solution at this point in the process, and so reduce the incidence of blooming and blistering. Experimenting with longer flash-dry times, perhaps with some assisted air movement, during times when these defects are common would not be too difficult with the existing setup and may prove enlightening. Experimenting with reducing the temperature in the drying tunnels to slow skinning and alleviate blistering may also be worthwhile.

To completely understand the drying process and fine tune the equipment for the coatings in use requires a considerable amount of further work in both the modelling and experimental fields, and an experimental dryer with air temperature and velocity controls would be needed.

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