CASE STUDY

A STUDY IN ORANGE * AN INVESTIGATION INTO PAINT DRYING

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It has often been said that one of the most boring human activities is watching paint dry. However, to coin another phrase, “Someone’s got to do it”; or have they?

When paint is freshly applied to a surface it does not have a silky smooth finish as would be desired. What this fresh coating surface looks like immediately after application, is a streaky set of “tramlines” if applied by brush or roller, or it has the dimpled and mottled appearance of orange peel when applied by spray. A study of car coatings in a car park or the coating surface of domestic appliances will demonstrate what this looks like, and generally it is not desirable. The cause of the problem is not immediately apparent and does not necessarily concern us here; what we want to know is how to get rid of it.

The answer to this is to design the paint so that it has the correct viscosity or rheology so that over a short period of time the paint can both dry, or set, and flow sufficiently to produce a flat featureless surface. Working together with colleagues at Safinah Ltd. and with scientists and technologists at Jotun Paints, we developed a method of calculating how a paint dries from measured rheological information.

A MODEL OF ORANGE PEEL

The basic premise is simple: an orange peel surface consists of peaks and troughs so that in a coating this corresponds to a region of relatively thin film coating, a trough, and a region of relatively thick coating, a peak.
Let us assume, to a reasonable first approximation, that these peaks and troughs are connected in a way described by a sine wave (figure 1). We now have a regular, easily defined profile of the depth of the coating on a surface.

The wavelength, λ, the amplitude, a, and the average film thickness, h, are defined in figure 1. It is easily seen that if the coating is a thin enough fluid, or has a low enough viscosity, η, the peaks will flowout into the troughs, and after a sufficiently long time the surface will become smooth. However, it is not gravity which is the major driving force to flow out, it is the surface tension, γ, which acts to reduce the total surface energy by minimising the surface area. It turns out that this is the main driving force for flow and levelling, and since the increment in surface tension is small as the coating approaches a smooth surface, the driving force is also small. The result of this is that the coating can never be perfectly smooth and there will always be some residual undulation, albeit very small if the paint is well formulated. The decay in the amplitude, a, from a_0 initially, with time, t, is exponential, hence:

Equation 1:

$$a = a_0\exp\{-\xi t\}$$

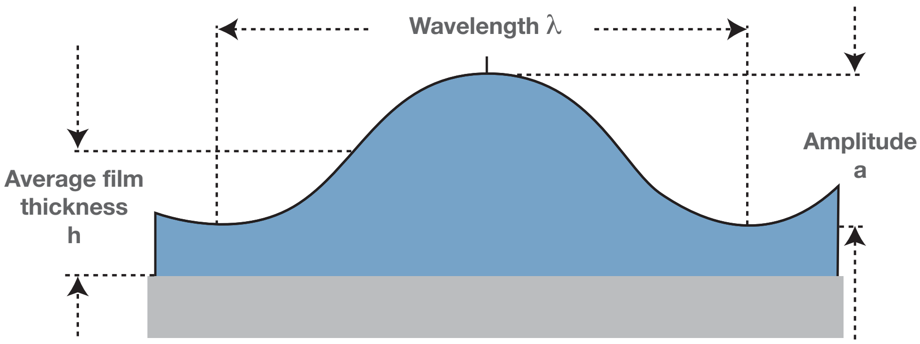

Figure 1. Model of a surface undulation, a sine wave, representing an orange peel coating.

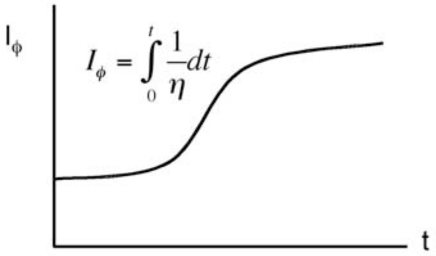

Figure 2. Integrated fluidity with time.

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* With apologies to Sir Arthur Conan Doyle
– A Study in Scarlet

The function ξ contains the driving force i.e. γ, the surface tension, and the retarding force i.e. η, the viscosity, and it also includes the geometric construction of the model.

Equation 2:

$$\xi = \frac{\gamma h^3}{3}\left(\frac{2\pi}{\lambda}\right)^4 \frac{1}{\eta}$$

It can be seen from equation 2 that the system is very sensitive to both average film thickness, h, to the third power, and the wavelength, λ, to the inverse fourth power. This means that as the average film thickness becomes smaller, flow and levelling become much more difficult. Similarly, as the wavelength becomes longer, flow out becomes more difficult. Hence thick coatings tend to be smooth and appear glossy whereas thin coatings can give a surface with the appearance of orange peel. It is not always convenient, and certainly costs more, to use a thick coating.

Queen Mary 2, painted by Jotun. Photograph courtesy of Carnival UK.

THE VISCOSITY PROBLEM

In equations 1 and 2 describing the flow out of the coating with time, the viscosity of the paint was simply described by η and appears as a constant. We know, however, that the viscosity of a paint when initially applied is reasonably low. We also know that the paint dries or sets, and at this point the viscosity is extremely high. So we know that the viscosity is changing as the coating dries and this will clearly affect the flow and levelling process. However, it is the fluidity, $1/\eta$, the inverse of the viscosity, which is used in the equations to describe the fall in amplitude with time. The paint goes from being a fluid material to being non-fluid, so this term drops from a finite value at t_0 to zero in the time-frame of the drying process.

Imagine that each very small step in time during the process contains an amount of flow; that is, each increment allows the coating to flow a certain amount. At the beginning of the process the flow is substantial and at the end of the process it is minimal, if any. If we add all these increments together we will arrive at the total amount of flow available for the process of flow and levelling. We are, in fact, integrating the fluidity over the time-frame of the process, hence:

Equation 3:

$$I_\phi = \int_0^t \frac{1}{\eta}\,dt$$

and we arrive at a term called the Integrated Fluidity, I_ϕ , shown schematically in figure 2.

We now have a method for calculating how well a coating will flow and level with

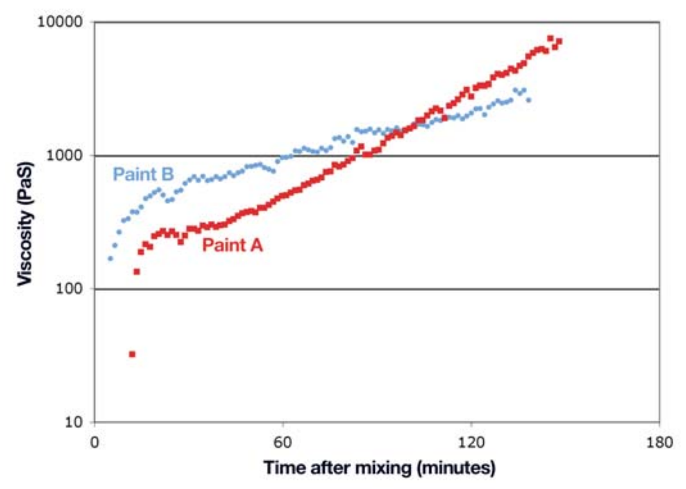

Figure 3. Viscosity from oscillation experiments, with time, for drying paints.

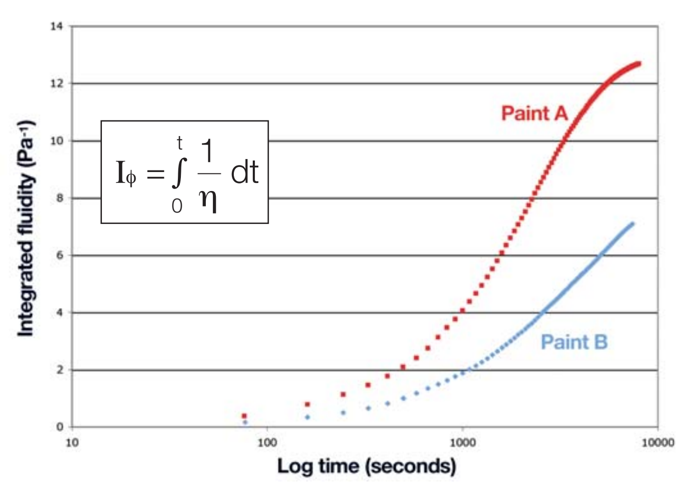

Figure 4. Integrated fluidity with time for drying paints.

time assuming we know how the viscosity changes with time, and we can measure the surface tension.

MEASURING A PAINT'S RHEOLOGY

Since viscosity, unless measuring a Newtonian fluid, is a function of shear rate or shear stress, and the process of flow and levelling is slow and unbounded, it is difficult to know how to measure the viscosity as it changes because we do not know the shear rate or stress. However, we do know that it is a slow process so we can make the assumption that all flow immediately after the application is in the Linear Viscoelastic Region. This means that we can measure the moduli (loss modulus – viscosity, and storage modulus – elasticity) of the coating as a function of time. Thus using a rheometer with a combination of oscillation experiments conducted on the drying coating, with small stress application and a medium oscillation frequency, the information required on the paint's linear viscoelastic behaviour can be obtained. The dynamic viscosity component, which is related to the shear viscosity, can then be extracted and used in the subsequent calculations.

CALCULATING THE FLOW AND LEVELLING PROFILE

Two paints produced by Jotun Paints, labelled here as A and B, were compared. Both show good application properties but have different in-service uses and require slightly different properties. The measured viscosity of the paints increases as a function of time, as the paints dry (figure 3). From this we can calculate the integrated fluidity (figure 4), which is also a monotonically increasing function with time, with paint A showing signs of levelling to a constant value.

Having obtained the integrated fluidity we can now use equations 1 and 2 to calculate the decay of amplitude with time. In the case of paint B (figure 5) it is immediately obvious that for the lower wavelengths, up to 4mm, the amplitude decays to zero in approximately 3000-4000 seconds. At the higher wavelengths, 5-10mm, there is a slow continuous drop in amplitude for periods of up to 10000 seconds (~3 hours). It is probable that the largest wavelengths will never flow out since the fluidity continues to decrease with time.

HOW DID WE DO?

A comparison of the amplitude decay of paint A with paint B for a number of wavelength undulations shows several features (figure 6). It is clear that paint A will flow out and level more rapidly than paint B. It is also clear that both paints show extremely good flow and levelling properties for the low wavelength undulations, which is in the region expected for surface defects on application, that is, in the region up to 5mm. Additionally, flow into small features on the subsurface being coated is also going to be rapid for these two materials. This is a consequence of the short time fluidity of the materials and is not a surface tension driven flow.

Longer time and longer wavelength data and calculations are very interesting; not only is paint A more fluid over the time for drying than paint B, as illustrated by the integrated fluidity, but it also has a greater rate of drying and therefore a more rapidly reached point when the paint can be safely called 'dry'. This may also lead to shorter overcoating intervals.

So how did we do? Both paints show good flow and levelling, and flow into small surface features such as cracks and holes, giving a smooth surface appearance rapidly. Paint A dries more quickly than paint B. Since the calculations used the same average film thickness for each paint, this may not lead to a good comparison, since a thinner coating of paint A will give similar properties to a relatively thicker coating of paint B. However, the paints are formulated for different purposes and for coating different surfaces. In conclusion, the calculations we performed are a good fit with commercial observation and practice, so we think we did very well indeed! ◆

With many thanks to Safinah Ltd. and Jotun Paints for permission to publish this article.

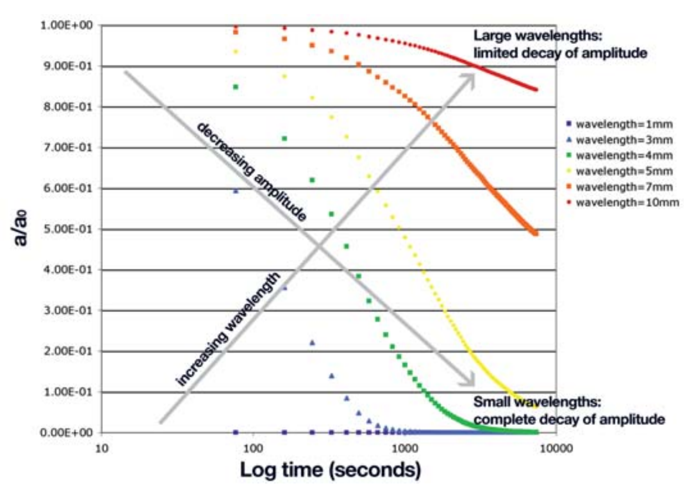

Figure 5. Amplitude decay with time for paint B.

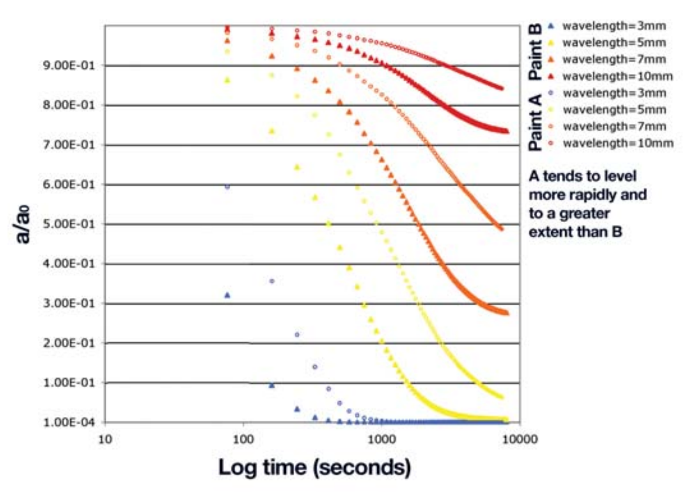

Figure 6. Comparison of amplitude decay for paints A and B.