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A mathematical model for drying paint layers

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Abstract. Many industrial processes involve the coating of substrates with thin layers of paint. This paper is concerned with modelling the variations in layer thickness which may occur as a paint layer dries. Firstly, a systematic derivation is provided of a model based on classical lubrication theory for a drying paint layer consisting of a non-volatile resin and a volatile solvent. The effects of variable surface tension, viscosity, solvent diffusivity and solvent evaporation rate are all included in the model. This analysis makes explicit the validity of the physically intuitive approximations made by earlier authors and hence clarifies when the model is appropriate. Secondly, the model is used to analyse the evolution of small perturbations to the thickness of, and the concentration of solvent in, a drying paint layer. This analysis provides an analytical description of the 'reversal' of an initial perturbation to the thickness of the layer and the appearance of a perturbation to an initially flat layer caused by an initial perturbation to the concentration of solvent. Thirdly, it is shown how a simplified version of the model applicable to the case of surface-tension-gradient-dominated flow can be derived and solved as an initial-value problem. Fourthly, the applicability of the present theory developed for solvent-based high-gloss alkyd paints to waterborne coatings is discussed. Finally, the results obtained are summarised and the practical implications of the work are discussed.

Key words: mathematical modelling, thin viscous films, surface-tension gradients, paints, coatings.

1. Introduction

Many industrial processes involve the coating of substrates with thin layers of paint. In this paper we model the variations in the thickness of the layer which may occur as a paint layer dries. Typically, as a layer of paint dries, any non-uniformities in the inital layer thickness die out under the action of constant surface tension, eventually leaving a layer of almost uniform thickness. This levelling motion is described in the early work of Smith, Orchard and Rhind-Tutt [1] and Orchard [2]. However, the experiments described by Overdiep [3, 4] show that some solvent-based high-gloss alkyd paints can exhibit more unusual behaviour as they dry. Firstly, the experiments showed an initially faster rate of levelling than that expected due simply to constant surface-tension effects. Secondly, and much more unexpectedly, after several minutes the paint surface underwent 'reversal'; that is, the original peaks became troughs and the original troughs became peaks. Recent experiments by Kojima, Moriga and Takenouchi [5, 6] show the same behaviour in waterborne coatings with high volatility (compared to water) co-solvent. Overdiep [3, 4] was the first to suggest that the presence of surface tension gradients might provide an explanation for both these phenomena. As

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Kornum and Raaschou Nielsen [7] describe, solvent-based high-gloss alkyd paints consist of a non-volatile resin dissolved in a volatile solvent. Since the surface tension of pure resin is higher than that of pure solvent, the surface tension of the layer is a decreasing function of the local concentration of solvent. As the solvent evaporates and the layer begins to level under the action of an initially uniform surface-tension force, the concentration of solvent near the peaks relative to the concentration near the troughs increases and hence the surface tension at the peaks becomes lower than that at the troughs. The resulting gradient of surface tension drives a flow from the peaks to the troughs which enhances the levelling process. The imbalance in the concentration of solvent is still present when the paint surface becomes level, and so surface-tension gradients continue to drive the flow and cause the observed reversal. The phenomena described above are caused by initial non-uniformities in the layer thickness. However, any initial non-uniformities in solvent concentration will also drive a flow which will produce non-uniformities in the thickness of even an initially flat layer.

Overdiep [3, 4] proposed a simple yet effective model for a drying paint layer which included the effect of variable surface tension caused by non-uniformities in the concentration of solvent and was capable of reproducing the observed reversal. This model has been analysed and generalised by Wilson [8], Moriarty, Terrill and Wilson [9] and Schwartz and Eley [10], who found good agreement between analytical and numerical calculations made, using the model and the experimental results for a planar substrate. The extension of the model to include the effects of a curved substrate has recently been investigated by Weidner, Schwartz and Eley [11]. The general problem of flow in thin liquid films driven by surface tension and surface-tension gradients has been studied by many different authors in a variety of other physical contexts. Among these Burelbach, Bankoff and Davis [12] investigated the stability and possible rupture of evaporating and condensing films accounting for vapour recoil, thermocapillary and van-der-Waals effects, while Jensen and Grotberg [13, 14] analysed the spreading of both insoluble and soluble surfactant on thin films and De Wit, Gallez and Christov [15] investigated the dynamics of thin free films with insoluble surfactants.

In this paper we begin in Section 2 by providing a systematic derivation of a generalisation of Overdiep's [3, 4] mathematical model based on classical lubrication theory for a drying paint layer consisting of a non-volatile resin and a volatile solvent. The effects of variable surface tension, viscosity, solvent diffusivity and solvent evaporation rate are all included in the model. This analysis makes explicit the validity of the physically intuitive approximations made by earlier authors and hence clarifies when the model is appropriate. In Section 3 we use the model to analyse the evolution of small perturbations to the thickness of, and the concentration of solvent in, a drying paint layer. This analysis provides an analytical description of the reversal of an initial perturbation to the thickness of the layer and the appearance of a perturbation to an initially flat layer caused by an initial perturbation to the concentration of solvent. In Section 4 we show how a simplified version of the model applicable to the case of surface-tension-gradient-dominated flow can be derived and solved as an initial-value problem. In Section 5 we discuss the applicability of the present theory developed for solvent-based high-gloss alkyd paints to waterborne coatings. Finally, in Section 6 we summarise the results obtained and discuss the practical implications of the work.

2. Derivation of the model

We consider a two-dimensional situation in which the horizontal and vertical co-ordinates are denoted by x and y, respectively; with respect to these co-ordinates and to time, t, the free