

# Monitoring of thermally driven drying varnish kinetics

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**Abstract:** Time dependence of solvent mass loss taking place in drying varnish kinetics is investigated. A simplified theoretical model based on Fick's law is presented and its relation to actual polymer drying diffusion process is discussed.

**OCIS codes:** (160.0160) General; (160.5470) General [Polymers.]

## 1. Introduction

The understanding of polymerization processes taking place in drying ink and coatings is central for varnish industry. Despite the great deal of research, there has been controversy concerning the theoretical description of polymerization processes that take place in drying varnish. A variety of models have been proposed to address the kinetics of polymer cure that includes solvent diffusion and mass transport [1], cracking [2,3], deformation and stresses [4], and photo-induced polymerization [5-7].

Of special interest is the understanding of the drying process of ink that occurs at room temperature. By measuring the loss of solvent mass in time, we develop a simplified model consisting of a system of two coupled partial differential equations: 1) a phenomenological Fick's law which assumes that the gradient of solvent mass is proportional to local solvent mass and the local concentration of reactant polymer molecules and 2) the usual kinetic equation. Despite the dynamics of the actual polymerization being *thermally* driven, our model gives an analytical solution formally identical to a *photoinduced* process [5]. There is a connection between the two processes: it can be shown that a necessary condition for the diffusive (thermal) process and the phenomenological Fick's law be equivalent is that the gradient of reactant polymer molecules mass must be proportional to the local concentration of solvent, as long as the diffusion coefficient remains constant (eq. 3). The solvent and varnish that we used in the experiment seem to follow this condition and a very good agreement between the experimental data and our model is achieved (fig. 1).

## 2. Methods and Results

The solvent loss of a commercial varnish layer was monitored along 24 hours with an analytical balance (Shimadzu AUW 220D, 0.01 mg resolution) at room temperature ( $25.7 \pm 1.0$ ) °C and relative humidity of ( $51.8 \pm 4.5$ ) %. To assure a uniform film thickness, two cylindrical metallic guides with 510  $\mu\text{m}$  diameter and 2 cm length were fixed 2 cm apart each other on the surface of a glass plate. A varnish film was spread across the space between the cylindrical guides with the aid of glass slide. After drying the varnish film reduced to a thickness of about 130  $\mu\text{m}$ . Figure 1 shows the experimental data (circles) of varnish film mass and the theoretical adjust (red line) from our model (eq. 4) along the drying process.

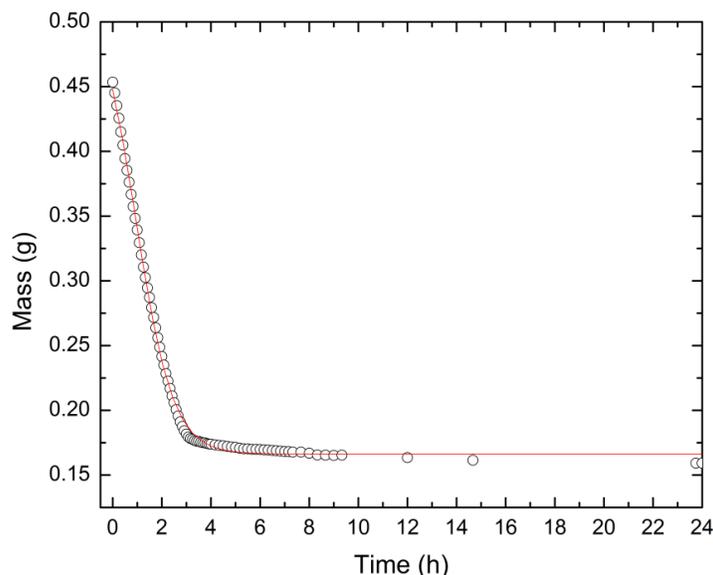


Fig. 1: Time film mass along the varnish drying

### 3. Modeling

Our simplified model makes use of phenomenological Fick's law coupled to the kinetic equation to describe the time and position (depth) dependence of the solvent mass  $S(x, t)$  and polymer mass  $C(x, t)$  during polymerization process,

$$J_n = \nabla_n S(x, t) = -\alpha \cdot C(x, t) \cdot S(x, t) \quad (1)$$

$$\frac{\partial C(x, t)}{\partial t} = -k \cdot \alpha \cdot C(x, t) \cdot S(x, t) \quad (2)$$

respectively, where  $k$  is a constant,  $\alpha$  is the absorption coefficient and  $\nabla_n S(x, t)$  stands for the normal component of the solvent mass gradient.

Despite our drying process being purely thermal, one has not made use of the diffusion equation for the solvent mass dynamics; instead one has used equation Fick's law (1). It is easy to show that, in the presence of kinetic equation (2), a necessary condition for the Fick's law and the diffusion equation be equivalent is

$$S(x, t) = \frac{D}{k} \cdot \nabla_n C(x, t) \quad (3)$$

where  $D$  is the diffusion coefficient assumed to be constant in the time interval over which the experiment was done.

The analytical solution for  $S(x, t)$  from system (1) and (2) is

$$S(x, t) = a + \frac{S_0}{1 + e^{-\alpha S_0 x (e^{kat} - 1)}} \quad (4)$$

where  $a$  is the final concentration of solvent and  $S_0$  is its initial mass. We find that Equation (4) fits experimental data (red line in fig. 1) very well for the set  $S_0 = 0.281 \text{ g}$ ,  $\alpha = 0.033 \text{ mm}^{-1} \text{ g}^{-1}$ ,  $k = 0.680 \text{ g mm min}^{-1}$  and  $a = 0.166 \text{ g}$  for  $0 \leq x \leq 0.1 \text{ mm}$  (equation (4) is fairly insensitive to depth  $x$ )

### 4. Conclusions

An analytical solution from a simplified model based on a phenomenological Fick's law and the kinetics equation is presented and describes rather well the loss of mass solvent during thermal polymerization process. Information of physical properties of both solvent and polymer, such as absorption and diffusion coefficient, can be obtained from the values of the free parameters (eq. 4) used to fit the experimental data.

### Acknowledgement

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