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Citation for published version (APA):

Erich, S. J. F., Laven, J., Pel, L., Huinink, H. P., & Kopinga, K. (2005). Dynamics of cross linking fronts in alkyd coatings. *Applied Physics Letters*, 86(13), 134105-1/3. Article 134105. <https://doi.org/10.1063/1.1886913>

DOI:

[10.1063/1.1886913](https://doi.org/10.1063/1.1886913)

Document status and date:

Published: 01/01/2005

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Dynamics of cross linking fronts in alkyd coatings

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(Received 2 November 2004; accepted 1 February 2005; published online 21 March 2005)

The dynamics of the curing process of alkyd coatings is an important aspect for coating performance. The formation of cross links in an alkyd coating film has been followed in time using a microimaging nuclear magnetic resonance setup, having a spatial resolution of $5\ \mu\text{m}$ perpendicular to the film. During this cross-linking process a front has been observed inside the coating film. The position of this front varied with the square root of time. With the help of a simple reaction model, we have proven that this dynamics results from the fact that the curing rate is limited by the oxygen flux into the coating. This model can also explain the differences in curing rates observed for various coatings. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886913]

Legislation concerning the use of coatings with volatile organic components (VOC) drives coatings manufacturers to focus on the production of water-borne coatings. Much research is done to develop water-borne coatings with the same performance as their solvent-borne counterparts. An important aspect of a coating is its network structure and the development of this structure during the drying process. Techniques to probe the spatial and temporal evolution of the coating structure are essential. Most available techniques are optical techniques, e.g., confocal Raman microscopy (CRM), which can be used to obtain spatially resolved chemical information. Recently, new techniques using high spatial resolution nuclear magnetic resonance (NMR), e.g., GARField¹ have become available for research and characterization of thin layers of hydrogen containing materials. These NMR setups can be used to measure the spatial and temporal evolution of the structure of a thin coating film, with a high spatial resolution perpendicular to the film layer. A major advantage of NMR over any optical technique is that also nontransparent coatings can be imaged.

An important class of commercially available paints contain alkyd resins. These resins consist of polymers with unsaturated fatty acid side chains. In recent years the drying process of alkyd resins has been studied extensively.²⁻⁷ The drying process of these resins consists of two stages. First, the solvent evaporates (physical drying) and next a network is formed by chemical reactions of double bonds (curing). In previous work it has been shown that both stages can be studied with NMR.^{3,4,7} In this letter we study the dynamics of the observed cross-linking fronts and explain it with a simple model.

The measurements were performed with a microimaging NMR setup, consisting of an electromagnet with specially shaped pole tips (GARField), generating a magnetic field of 1.4 T with a gradient of 36.4 T/m perpendicular to the coating film. The NMR pulse sequence used to obtain the hydrogen density profiles and the signal decay is an Ostroff-Waugh⁸ sequence ($90_x^\circ - \tau - [90_y^\circ - \tau - \text{echo} - \tau]_n$). The interecho time (2τ) used in the experiments equals 200 μs . The spatial resolution is $5\ \mu\text{m}$. The acquisition of each profile took about 10 min, using 512 signal averages. The ex-

periments were performed on two alkyd samples: a water-borne sample and a commercially available solvent-borne sample. Both coatings were cast on a $100\ \mu\text{m}$ cover glass sheet, using a $200\ \mu\text{m}$ spiral application rod.

The water-borne system is an emulsified alkyd resin mixed with NuoDex WebCo 8%, as a catalyst. The profiles of this water-borne sample are shown in Fig. 1. At the right edge of the profiles the glass sheet is located. The first three profiles show the evaporation stage, during which the solvent evaporates and the coating shrinks. The vertical dashed line corresponds to the position of the surface of the coating after evaporation. After this evaporation stage, a front forms and moves away from the surface of the coating towards the glass sheet. The observed front arises from a NMR signal loss due to fast signal decay in the cured regions. This corresponds to the formation of a cross-linked network, as has been proven by comparing NMR with confocal Raman microscopy (CRM).⁷ After a certain time a layer at the top of the coating has cross-linked; this layer is often called a skin.

The profiles of the solvent-borne sample are shown in Fig. 2. Again the first profiles show the evaporation stage. The vertical dashed line shows the position of the surface of

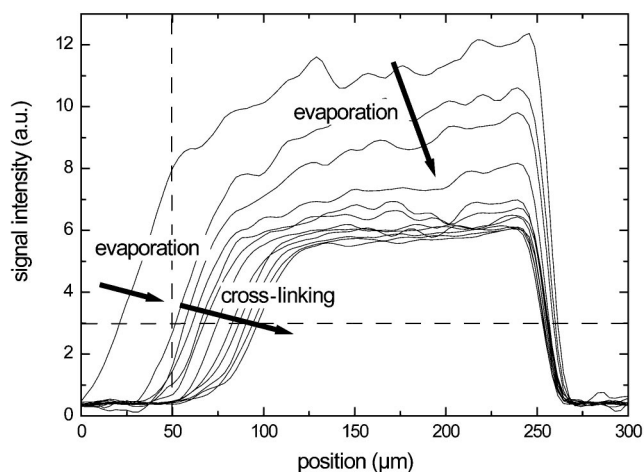


FIG. 1. NMR hydrogen profiles of a water borne alkyd sample during drying. The left side is the top of the coating, at the right the cover glass is located. The vertical dashed line shows the top of the film after evaporation. The profiles are plotted for 0, 1.25, 2.5, 5, 8, 10.5, 26, 53, 79, 105, 132, and 158 h.

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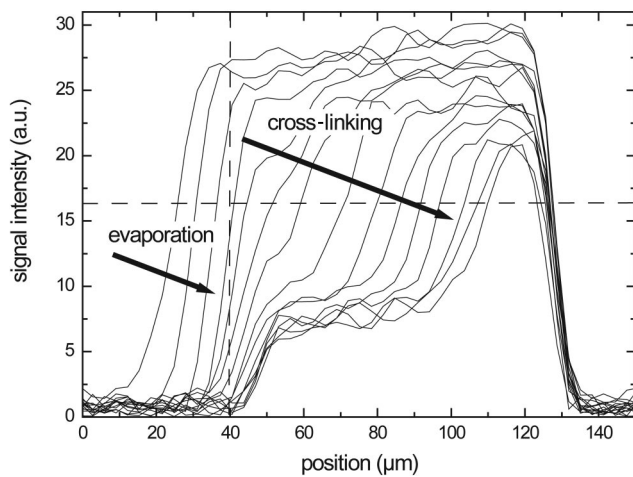


FIG. 2. NMR hydrogen profiles of a solvent-borne alkyd sample during drying. The left side is the top of the coating, at the right the cover glass is located. The vertical dashed line shows the top of the film after evaporation. The profiles are plotted for 10, 20, 30, 50, 70, 90, and 120 min. After the seventh the profiles are plotted for every 3 h, 20 m.

the coating after evaporation. Note that in this system the signal has not completely vanished after the cross-linking front has passed. This is caused by the fact that the network is not as rigid as in the water-borne sample. CRM measurements have shown that the network has indeed only partially cross-linked.⁷ We will return to this observation later on.

In order to characterize the dynamics of the curing front, we have determined the front positions f from the intersections of the fronts visible in the different profiles with the horizontal dashed line. For both samples we place this horizontal dashed line about half the height of the front. The moment that the front forms and starts to move into the coating we will refer to as $t=t_0$. The position of the front at $t=t_0$ is denoted by f_0 . The front positions f obtained for both samples are plotted in Fig. 3 as $(f-f_0)^2$ against $t-t_0$. This figure reveals that within experimental inaccuracy the front position varies with the square root of time in both the water borne and the solvent borne system.

To explain this front movement $f \sim \sqrt{t-t_0}$ the following model is used. We consider a plane of thickness dx at position x within the coating film. The coating consists of unsaturated fatty acids with a certain density ρ_d of double bonds.

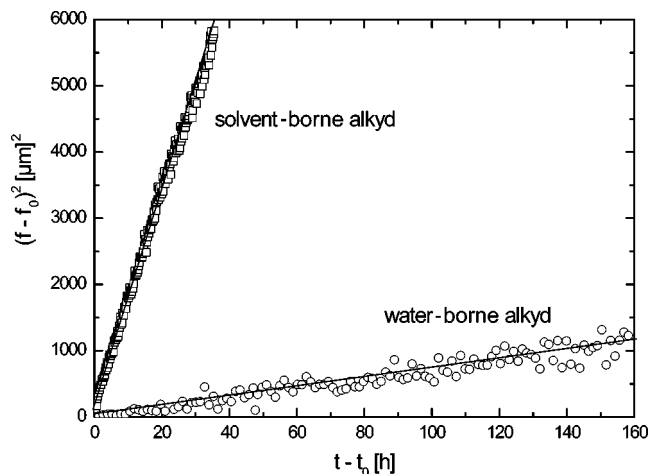


FIG. 3. Squared front position against time, for a solvent-borne and water-borne alkyd system.

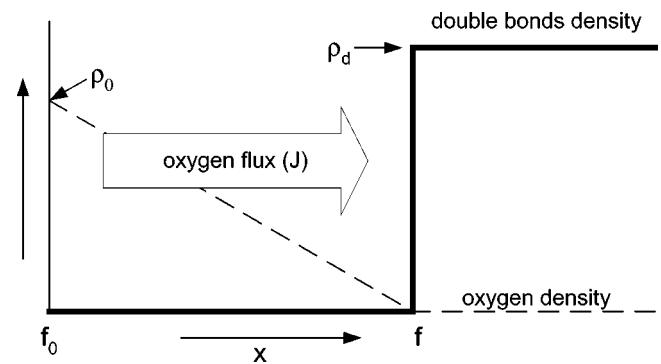


FIG. 4. Schematic representation of the drying model. The dashed line indicates the oxygen density. The black line indicates the amount of double bonds. At the curing front the oxygen density is zero, due to the high reaction rate.

A certain amount n of oxygen molecules are consumed per double bond during the cross-linking process, and a fraction ϕ of the bonds is used during the cross-linking process. The cross linked volume per mole oxygen is given by $\nu = 1/n\phi\rho_d$. We assume that the reaction rate is very high, which means that the oxygen flux into a small layer at position x at a time t will instantaneously be used for the cross-linking reaction, until all possible oxygen reaction sites have vanished. At that moment, the front has passed this position. The speed of the front movement is therefore given by

$$\frac{df}{dt} = \nu J, \quad (1)$$

where J (mol/m²s) is the molar flux of oxygen. The flux of oxygen in the cross-linked region is given by

$$J = -D \frac{d\rho}{dx}, \quad (2)$$

where D (m²/s) and ρ (mol/m³) are, respectively, the diffusion constant and the molar density of oxygen in the cross-linked region. Since the surface of the coating is in equilibrium with the surrounding air, the oxygen density ρ_0 in the surface layer of the coating film will be constant. Because we assumed that at the front all oxygen is consumed instantaneously, the oxygen density equals zero at the front. Furthermore, we assume that the oxygen flux is constant in the cross-linked region. This assumption is valid because the amount of oxygen lost in this region is negligible. In addition, the oxygen distribution is assumed to adapt itself immediately to changes of the front position, resulting in a quasi-steady-state approach for the oxygen distribution. With these assumptions the oxygen density linearly decreases over the cross-linked region, see the schematic diagram of our model in Fig. 4. Equation (2) can now be rewritten as

$$J = D \frac{\rho_0}{f(t) - f_0}. \quad (3)$$

When Eqs. (1) and (3) are combined, the following expression for the front position can be obtained:

$$f(t) = f_0 + \sqrt{2\nu D \rho_0 (t - t_0)}. \quad (4)$$

This equation is in agreement with the observed behavior. This suggests that the oxygen supply is indeed the key factor

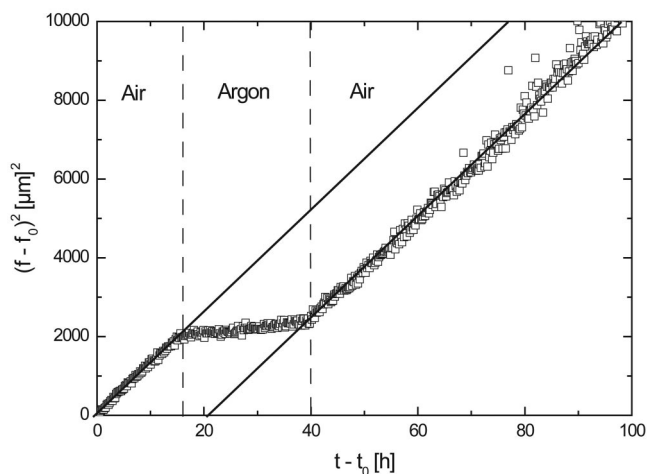


FIG. 5. Squared front position against time for the solvent-borne alkyd system. After 18 h of drying an argon atmosphere was created above the film. At $t=40$ h the air atmosphere was restored.

limiting the rate of the curing process, and not the capacity of the catalyst.

To check this model we have performed an experiment in which the oxygen supply was limited by creating an argon atmosphere above the coating film. The results of this experiment are shown in Fig. 5. At $t-t_0=18$ h essentially all oxygen was removed above the film. The front stops, which indicates that the chemical reaction stops. It appears that only a few minutes are needed to deplete the oxygen inside the cross-linked region. This justifies the quasi-steady-state approach for the oxygen distribution. When 22 h later ($t-t_0=40$ h) the argon atmosphere is removed and the air atmosphere is restored, the front movement returns to its original speed. This experiment unambiguously demonstrates that oxygen supply is the limiting factor for the reaction and proves the validity of our model.

Equation (4) also explains the higher front speed of the solvent-borne coating compared to water-borne coating (see

Fig. 3). The difference of oxygen density in the surface layer ρ_0 between both coating systems is expected to be small. However, the diffusion and cross-linked volume per mole oxygen vary significantly. One expects an increase of the diffusion constant in a system with a higher polymer mobility in the polymer matrix, which is the case for the solvent-borne system compared to the water-borne system. As we have already noted, the NMR signal from the solvent-borne sample remaining after cross-linking indicates this higher mobility. Furthermore, this solvent-borne system was known to have a smaller fraction ϕ of double bonds used during the cross-linking process,⁷ which also indicates a higher polymer mobility. Since less double bonds have cross-linked, the cross-linked volume per mole oxygen ν is also higher. Hence, the factor $\nu D \rho_0$ [Eq. (4)] is higher in the solvent-borne system, which agrees with the higher curing rate, observed in Fig. 3. This shows that our model can also be used to explain the difference in curing rates of coatings which are limited by oxygen diffusion.

This research was financially supported by the Center for Building and Systems TNO-TUE.

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