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EVALUATION OF THE DRYING PROCESS OF SOME VARNISHES AND PAINTS APPLIED ON FIR WOOD

BY

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Abstract. Given the growing interest shown by the population in the restoration and redecoration of their dwelling spaces, wood is a material that has been increasingly used both in exterior constructions and for interior finishing works. The most important stage in the obtaining of a coat of paint able to protect wood is the drying process, which results in a coat of paint, called film, which strongly adheres to the surface of the wood. In order to analyze the drying process and to determine the effective diffusion coefficients, respectively, we applied three types of alkyd paint available on the market: a Teflon protective varnish (SLT), yacht varnish (LYP) and superglossy enamel (ESI) on dried fir-wood disks which were 5 mm in diameter. The drying process and the formation of the film itself were achieved using a Mettler Toledo TGA-SDTA851^e device, under constant temperature. The effective diffusion coefficient values obtained ranged between $0.4{\cdot}10^{-12}$ and $2.4\ {\cdot}10^{-12}$ m^2/s. The theoretical models achieved show higher deviations in the case of the SLT samples. The cause of these deviations may be the complex composition of the paint film but also the fact a "skin effect" film is formed after drying at linear decreasing speed, which prevents solvent diffusion.

Keywords: Paint; drying process; effective diffusion coefficient; theoretical models; skin effect.

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1. Introduction

Wood has been used as a building material since the beginning of human civilization, since a wood dwelling provides comfort, that is it is warm in winter and cool in summer. The flexibility of the wood makes these buildings to react adequately in case of vibrations and earthquakes. Wood has also been used a lot in the furniture industry, as well as to manufacture many other objects that are just as important and useful to humans: kitchen ustensils, gardening tools, wooden packages and boxes, barrels for maturing drinks, etc. Many art objects and musical instruments that bring excitement and beauty to people's lives are also made of wood. Varnishes and paints are used to protect and embellish wood. Paints cover and color wooden surfaces, whereas varnishes form transparent films and coatings that preserve their natural appearance. An important step in obtaining a film able to protect wood exposed to the weather is the drying process (Giraud *et al*., 2008; Kadoura *et al*., 2016). Our research group has recently suggested a simple and accurate method of evaluating the drying process of some varnishes and paints with the help of the Mettler Toledo equipment (Mihailă *et al*., 2019a; Mihăilă *et al*., 2019b). In this study, we will determine the effective diffusion coefficients of the drying process of three types of alkyd paint available on the market: a Teflon protective varnish (SLT), yacht varnish (LYP) and super-glossy enamel (ESI) applied to 5 mm-diameter dry fir wood disks. The actual film-forming process, *i.e.* obtaining a film strongly adhering to the surface of the wood, was carried out using the Mettler Toledo TGA-SDTA851e equipment, under constant 25°C temperature, using synthetic air with a flow rate of 20 mL/min as a drying agent. The evaluation of the behavior of the varnish or paint film during the drying process is the real basis of calculation for industrial dryers, as the only way determination method is the experimental one. The factors that influence the moisture and solvent evaporation process vary in space and time and the film subjected to drying changes its characteristics during the process.

Chen *et al*. used thermogravimetric analysis equipment to analyze the kinetics of the poplar sawdust drying process at four temperatures 60, 70, 80 and 90°C. They calculated the effective diffusion coefficients and the activation energy for the sawdust drying process, which took place mainly at decreasing speed (Chen *et al*., 2012a). The effective moisture diffusion coefficients during the drying process of certain foods were determined with a piece of thermogravimetric analysis equipment by Joardder *et al*. (2014) and by Cheng *et al.* (2012b). The kinetics of the drying process of some thin films of polymers of pharmaceutical use was comparatively analyzed using a piece of Q5000 TGA equipment and a convective drying laboratory device by Velaga *et al*. Their study showed that the TGA method may be used as a simple and accurate tool to design the drying process of thin films. The results provided important insights into the drying processes of thin polymer films that are relevant to both the pharmaceutical and food and materials industries (Velaga *et al*., 2018).

A detailed analysis of the drying process of some polymeric paints in a laboratory device was also conducted by Dubreuil *et al.* They calculated the effective diffusion coefficients and found that the drying process of most varnish or paint coatings involves two different regimes: first a quick process involving solvent exchanges between the solution and the environment and then a period during which the solvent evaporation flow decreases significantly, and the kinetics of the process becomes governed by the physico-chemical properties of the system (Dubreuil *et al*., 2002). Forţu *et al.* analyzed the influence of the main factors that contribute to the drying of polymeric films in a laboratory device with drying tunnel. They showed that the drying of the polymer film was influenced by both the temperature and the speed of the gas, and also by the ‘skin’ effect that may occur at the fluid-gas interface. If this effect occurs, the mass transfer from the liquid phase to the gas phase decreases as a result of the sharp decrease of the effective diffusion coefficient (Forţu *et al*., 2019).

This paper aims at calculating the effective diffusion coefficients in the actual film-forming process for a series of varnishes and paints available on the market, using a Mettler Toledo TGA-SDTA851e derivatograph and applying the analytical solution of Fick’s equation for the ‘thin plate’ case suggested by Cranck for long solvent removal times (Cranck, 1975). To this end, the three types of paints available on the market, a Teflon protective varnish (SLT), yacht varnish (LYP) and super-glossy enamel (ESI), were applied in a thin layer on 5 mm-diameter dry fir disks. The drying process was carried out under constant 25°C temperature, using synthetic air with a flow rate of 20 mL/min as a drying agent. The flexibility of dry varnish and paint films was studied using a Mettler Toledo DSC1 piece of equipment, by determining the glass transition temperature (T_g).

2. Materials and Methods

We studied the drying process of three types of alkyd paint available on the market: a Teflon protective varnish (SLT), yacht varnish (LYP) and super-glossy enamel (ESI) with a Mettler Toledo TGA-SDTA851e piece of equipment. This was conducted for two hours under constant 25°C temperature, using synthetic air with a flow rate of 20 mL/min as a drying agent. The different types of varnish or paint that we analyzed were applied on 5 mm-diameter dry fir disks in thin 0.10 to 0.23 mm layers. All the coating products had alkyd resins, in addition to which the yacht varnish had urethane components, and the SLT protective varnish had Teflon. The super-glossy enamel marked ESI is a coating product based on fatty alkyd resins and has a black hue. The LYP varnish is transparent, whereas the SLT varnish has a mahogany hue. All three coating products may be used both indoors, where they are not subject to the action of any environmental factors, and outdoors without undergoing changes due to the action of environmental factors (precipitation, humidity, sun radiation, wind, freeze-thaw cycles) for a particular period of time guaranteed by the manufacturers.

The differential scanning calorimetry (DSC) curves, for dry paint films removed from the wooden disks using a cutter, were recorded using the Mettler Toledo DSC1 equipment, in an inert atmosphere, at a heating rate of 10°C/min. Scanning was performed within the -80 to 200°C temperature range, two heating and one cooling cycles. The mass of the samples encapsulated in aluminum pans having pierced lids to allow the evaporation of the volatile components ranged between 1.9 and 4.6 mg.

The STARe software version 9 of Mettler–Toledo was used to assess the thermogravimetric (TG) and (DSC) curves.

3. Results and Discussions

Percentage thermogravimetric curves recorded at 25°C in the Mettler Toledo TGA-SDTA851^e equipment are shown in comparison in Fig. 1. We found solvent contents of 48.43% and 49.24% in the SLT and ESI samples, respectively; as for the alkyd varnish which also contained urethane components, the solvent content was 40.53%. Based on these thermogravimetric curves, the MR (Mihailă *et al.*, 2019a) - mass of residual normalized solvent - was calculated, and the findings were used to evaluate the effective diffusion coefficients.

In this study, the effective diffusion coefficients (D_{eff}) were determined taking into account the analytical solution of Fick's equation, for different geometric shapes (Vasić *et al.*, 2012), especially for the ‘thin plate’ case developed by Cranck, considering the dependence on lengthy solvent removal times, in the ratio Eq. (1) (Cranck, 1975):

$$\ln\left(\frac{\pi^2 MR}{8}\right) = -\pi^2 \frac{D_{eff}}{\delta^2} t \qquad (1)$$

where: δ is the thickness of the varnish or paint film on the wooden disk, MR - mass of residual normalized solvent, and t time. Please note that the solvents were thought to have been carried through diffusion, and the temperature and diffusion coefficients were thought to have constant values.

According to the graphical representation $\ln\left(\frac{\pi^2 MR}{8}\right) = f(t)$ in Fig. 2, straight lines with negative slope and correlation coefficients greater than 0.996 were obtained for the three types of paints that we analyzed.

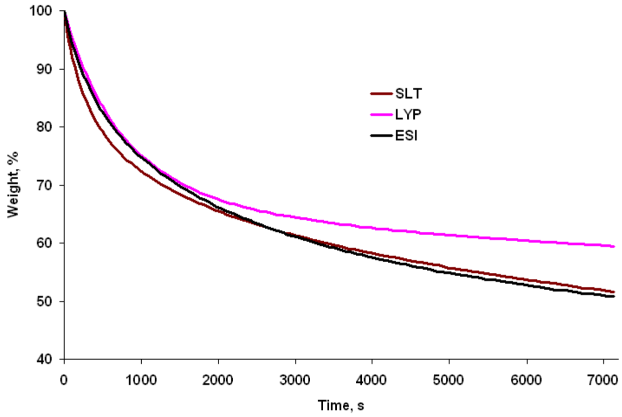

Fig. 1 − TG curves under constant temperature.

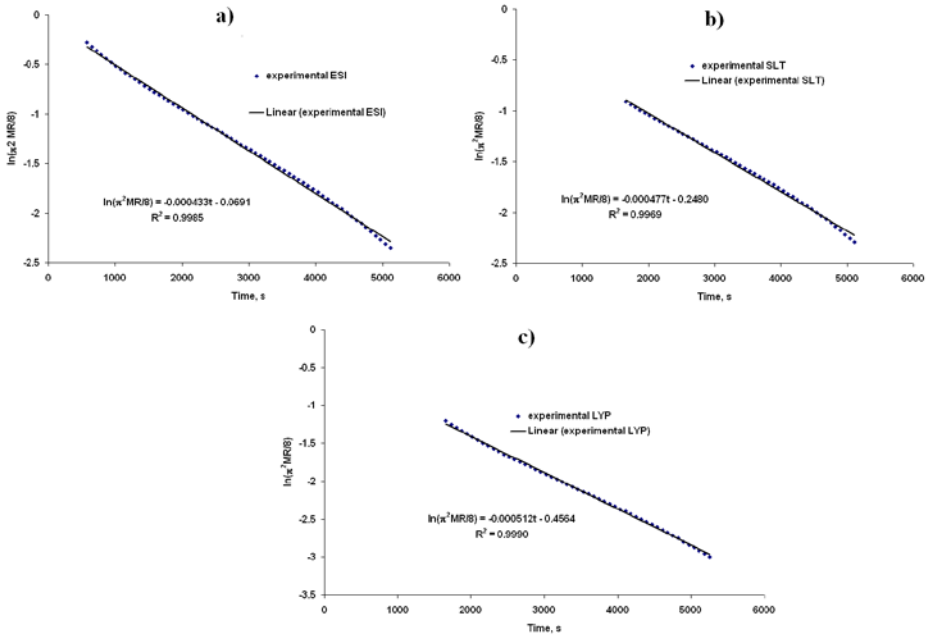

Fig. 2 − Calculation of effective diffusion coefficients.

Table 1 shows: correlation coefficients (r^2), varnish or paint film thickness on the fir wood disk (δ) and effective diffusion coefficient values (D_{eff}). The analysis of the obtained results revealed much higher values for the effective diffusion coefficient of the LYP varnish, which is transparent, than for the ESI enamel and Teflon protective varnish, which also contain pigments.

Table 1

Values of Effective Diffusion Coefficients

Sample	r^2	$\delta \cdot 10^3$ (m)	$D_{eff} \cdot 10^{12}$ (m^2/s)
ESI	0.9985	0.108	0.512
SLT	0.9969	0.109	0.466
LYP	0.9990	0.233	2.407

Solvent diffusion in the paint film and also its evaporation on the surface of the film are considered to be decisive stages of the drying process. The physical model of the drying of a film applied on a flat surface comprises two stages: - the *first stage* that may be revealed especially when drying films with a high solvent content and - *the second stage*, in which the process is also influenced by the diffusion coefficient in the film and the thickness of the film, respectively. Solvent evaporation in the first stage behaves similarly with pure solvent evaporation on a flat surface, and the diffusion coefficient in the film and the thickness of the film have no influence. The first stage may be missing when drying films with a low solvent content (Forţu, 2019). In view of the experimental measurements recorded at the beginning and at the end of the drying process and of the drying kinetics values obtained, we concluded that diffusion depended mainly on the solvent content of the paint sample. By means of an exponential equation, it has been shown that the diffusion process intensifies with the increase of the solvent content (Livian and Vergnaud, 1995).

On solvent diffusion into a polymer film during the second drying stage, the solvent transfer into the film may be thought to be the result of the equation that describes the variation of the solvent content with time deduced by Crank (1975) based on Fick's law.

$$MR = \frac{M(t) - M_e}{M_0 - M_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[- \frac{(2n+1)^2 \pi^2 D_{eff}\, t}{\delta^2} \right] \qquad (2)$$

where: MR – mass of residual normalized solvent, M_0 – initial solution mass, M_e – equilibrium mass of solution, M(t) – mass of solution at t time, δ – film thickness [m], t – time [s] , D_{eff} – solvent-film diffusion coefficient [m^2/s]. Please note that film thickness, effective diffusion coefficient and temperature are thought to be constant. If the first three items of the sequence in Eq. (2) are considered, then:

$$MR = \frac{M(t) - M_e}{M_0 - M_e} = \frac{8}{\pi^2} \left[e^{-D_{eff}\, t (\pi/\delta)^2} + \frac{1}{9} e^{-9 D_{eff}\, t (\pi/\delta)^2} + \frac{1}{25} e^{-25 D_{eff}\, t (\pi/\delta)^2} \right] \qquad (3)$$

Fig. 3 (*a*, *b* and *c*) shows the time-dependent variation of dimensionless residual moisture for the three ESI, SLT and LYP samples. The experimental data are compared with the simulated values based on the diffusion model Eq. (3). The model uses the values of the diffusion coefficients and the initial film thicknesses shown in Table 1.

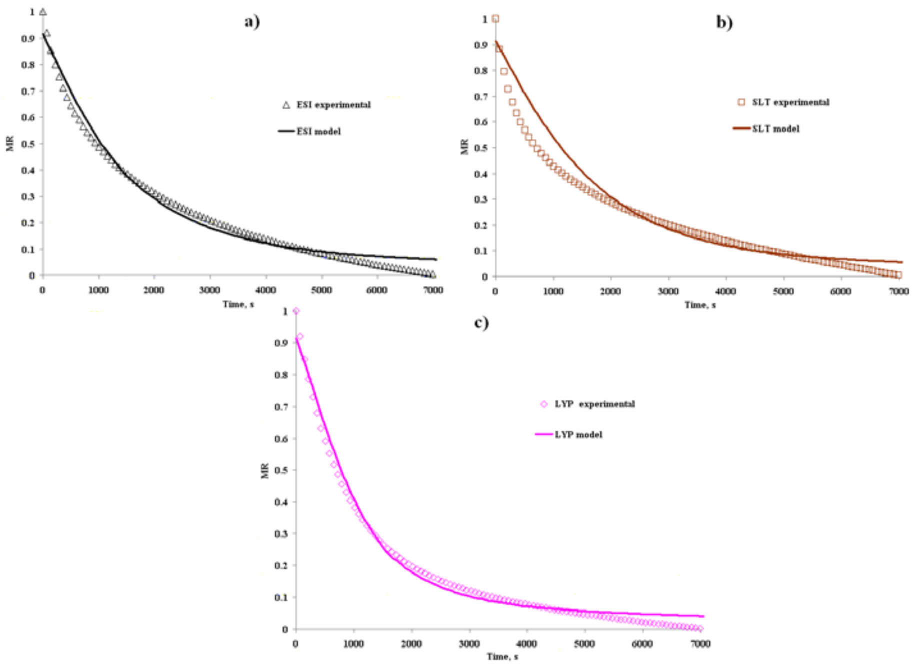

Fig. 3 − Time-dependent variation of dimensionless residual moisture.

The results obtained and shown in Fig. 3 (*a*, *b* and *c*) indicate a good correlation between the model and the experimental data in case of ESI (maximum deviation is ±17%) and LYP (maximum deviation is ±18%) drying. For the SLT, a satisfactory correlation was obtained (maximum deviation is ±22%). Larger deviations were detected in the protective varnish containing Teflon, in which the 'skin' effect on the film-gas interface is likely to occur. At the beginning of the drying process the solvent evaporation rate is high and then it decreases due to the 'skin' effect.

We may conclude that it is difficult to model the drying of paint films that have a complex composition with the help of classical models described in literature. The paint film may also contain a number of fillers that have a porous structure and obviously most often the solvent used is not a pure component.

The paint (SLT, ESI and LYP) films dried in the Mettler Toledo equipment and after having been kept under laboratory conditions (23 ± 2°C temperature and 40 ± 5% humidity) for two years were removed from the fir wood disks using a stainless-steel blade cutter and subjected to three heating/cooling cycles (2 heating and one cooling cycles) within the -80 to 200°C temperature range, using the Mettler Toledo DSC1 equipment. The glass transition temperatures shown in table 2 were obtained. Please note that they range between 10 and 20°C, values close to what other researchers have reported in literature for different alkyd resins derived from multifunctional glycolates: glycerol (G), diethylene glycol (DEG) and pentaerythritol (PE) (Spasojevic *et al*. 2015). We also found that the flexibility of the analyzed films did not change significantly even after being kept under laboratory conditions for two years.

Table 2

Glass Transition Temperatures of the SLT, ESI and LYP Samples

Sample	T_g (°C)[a]	T_g (°C)[b]
SLT	10.35	10.98
ESI	19.60	17.71
LYP	18.62	15.81

[a]dried in the Mettler Toledo equipment and [b]kept under laboratory conditions for two years

Evans *et al*. believe that glass transition temperature (T_g) may be used as an indicator of the coating film flexibility on wooden surface. If the application of varnishes and paints to wood surfaces is designed to allow that wood to be used outdoors, then they should possess and maintain relatively low T_g values (Evans *et al*., 2015). Schmid et al. analyzed the exposure behavior to outdoors conditions of two films, one with a glass transition temperature of 10°C and the other with 50°C. One year after outdoor exposure, they found the film with T_g = 50°C to have cracks, whereas the film with T_g = 10°C preserved its quality (Schmid, 1988). The same conclusions were reached by Nejad and Cooper, who concluded that the most important coating properties that have the greatest influence on the quality of certain alkyd paints used for wood protection under weather conditions are the film thickness and the glass transition temperature (Nejad and Cooper, 2011).

4. Conclusions

Our study describes a simple and accurate method for calculating the effective diffusion coefficients in the actual film-forming process for a series of varnishes and paints available on the market, using the Mettler Toledo TGA-SDTA851[e] derivatograph. The analytical solution of Fick's equation was applied for the ‘thin plate’ case proposed by Cranck for long solvent removal times. The effective diffusion coefficients obtained for the three types of paints available on the market, a Teflon protective varnish (SLT), yacht varnish (LYP) and super-glossy enamel (ESI) applied in a thin layer on 5 mm-diameter dry fir wood disks, ranged between $0.4 \cdot 10^{-12}$ and $2.4 \cdot 10^{-12}$ m^2/s. It has been shown that it is difficult to model the drying of paint films that have a complex composition, with the help of classical models described in literature. We found a good correlation between the model and the experimental data for ESI and LYP drying. Greater deviations were found in the case of the protective varnish containing Teflon, in which the 'skin' effect on the film-gas interface is likely to occur. The paint films (SLT, ESI and LYP) that we analyzed showed glass transition temperatures ranging between 10 and 20°C. The glass transition temperatures (T_g) that may be used as an indicator of the coating film flexibility on wooden surfaces do not change significantly even after being kept under laboratory conditions for two years.

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EVALUAREA PROCESULUI DE USCARE A UNOR LACURI ŞI VOPSELE APLICATE PE LEMN DE BRAD

(Rezumat)

Lemnul este un material care este din ce în ce mai mult utilizat atât în construcţii exterioare dar şi pentru finisaje interioare, datorită preocupării tot mai mari a populaţiei în reamenajarea şi decorarea spaţiilor de locuit. Cea mai importantă etapă în obţinerea unei pelicule de vopsea care să protejeze lemnul este procesul de uscare, în urma căruia se obţine o peliculă puternic ancorată pe suprafaţa lemnului, denumită film. Pentru analiza procesului de uscare, respectiv determinarea coeficienţilor efectivi de difuzie, s-au utilizat dischete de lemn de brad uscat cu diametrul de 5 mm pe care s-au aplicat trei tipuri de vopsele alchidice comerciale: un lac protector cu (SLT), un lac iaht lake (LYP) şi un email superlucios (ESI). Procesul de uscare, respectiv de formare a filmului propriu-zis, s-a realizat cu echipamentul Mettler Toledo TGA-SDTA851e, în condiţii de temperatură constantă. Valorile coeficientului efectiv de difuzie obţinute sunt cuprinse între 0.4·10-12 şi 2.4 ·10-12 m^2/s. Modelele teoretice construite dau abateri mai mari în cazul probei SLT. Cauza acestor abateri poate fi compoziţia complexă a peliculei de vopsea dar şi faptul că după perioada de uscare cu viteză descrescătoare liniară se formează o peliculă „skin effect”, care împiedecă difuzia solventului.