Monitoring drying process of varnish by immersion solid matching method

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Abstract

The characterization of the drying process of paints and coatings on the surfaces is important for many industrial applications. We present a new optical method to study the drying process of varnish based on immersion solid matching technique. The principle of the method is to match the refractive index of dry varnish with the added particles, making the dried varnish optically transparent. The state of the drying process can be evaluated by following the transparency of the varnish by visual inspection or imaging by camera. The method has several merits since it is non-contact, fast, simple and low-cost. In addition, particles that are invisible in dry varnish can provide improved properties such as hardness, abrasion and corrosion resistance or retard flammability without sacrificing the optical appearance of the coating.

Keywords: turbidity, refractive index, immersion method, drying process, coatings, CCD.

1. Introduction

Many industrial processes involve the coating of surfaces for the protection against corrosion or abrasion, the modification of mechanical properties, the improvement of waterproofness or adjusting the visual appearances (color, gloss, patterns etc.). The drying process of coatings is a complex phenomenon, which depends on factors such as temperature, humidity, airflow, chemical composition and physical dimensions [1]. The control of drying times has significant influence on the throughput of coating process thus making drying monitoring interesting from an economical point of view in particular. It is important to minimize the drying times of the coating layers in order to shorten the delay before adding the next coating layer [2] or continuing to the next process phase. Therefore, monitoring and understanding about the painting process are very important for coating manufacturers.

To monitor the changes in the physical and chemical properties of coatings have conducted by several techniques. Microscopy techniques such as electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) have typically used for the analysis of drying process of coatings [3]. In addition, some complementary drying monitoring techniques have been reported. These methods are based on reflection and the spectral analysis such as the diffusing-wave spectroscopy [2], interferometric technique [4], fiber Bragg grating sensor technique [1], refractometer technique [5], laser speckle image technique [3], terahertz technique [6], ultrasonic reflection method [7], and nuclear magnetic resonance technique [8]. Each of these techniques provides useful information on the drying process state. However, most of these methods are not suitable for monitoring manufacturing processes because they are time-consuming (requires vacuum), expensive and requires a high level of skill from operators [3]. Therefore, there is a need for a simple technique that would enable real-time and inexpensive drying process monitoring.

The aim of this study is to evaluate the capability of immersion matching method for varnish drying process assessment. The exploited immersion matching method relies on the refractive index match between the solid particles and the varnish. Immersion liquid method has been popular for the microscopic or spectrophotometric determination of refractive index of particles [9]. Conventionally the immersion liquid method follows a protocol where a set of immersion liquids with a priori known refractive indices are prepared. The idea of the new method is to match the refractive index of the added solid particles to the tested dry coating material, whereby the particle refractive index of particles is the same with the surrounding dry coating. At first, the suspension with particles is opaque (turbidity) because the particles scatter light due to index mismatch with the ambient coating materials in liquid phase. In the case of perfect refractive index match between the coating material and the particles, the coating suspension becomes transparent because the scattering approaches zero and consequently the light transmittance through suspension will be at its maximum [9]. This phenomenon enables easily to analyze when the paint is dry. The present method is not restricted to varnish only but is proposed to be applicable across a broad range of applications assuming the paint is clear or transparent.

2. Materials and methods

In this study, Mr. Color C46 Clear varnish (Transparent, by GSI Creos) was used. The varnish is composed of methyl isobutyl ketone (30-40%), ethyl acetate (5-10%), butyl acetate (5-10%), ethanol (1-5%), methyl ethyl ketone (1-5%), n-butyl alcohol (1-5%), and diacetone alcohol (1-5%). KCl powder was purchased from FF-Chemicals. The purity of the KCl sample was higher than 99.5%, but according to the product description it contained small amounts of Ca, Ba, Fe, Pd, Br, I and SO_4. The median particle size of KCl (on a volumetric basis) was 116 μm as measured by a Beckman Coulter LS 13 320 laser diffraction analytical device in acetone. The refractive index of KCl is 1.4856 at 589 nm [10].

The sample suspension consisted of 1002 mg of varnish and 155 mg of KCl powder. The suspension was mixed with the vortex mixer (Analog Vortex Mixer, VWR) for 2 min at speed setting of 10. The air bubbles, accumulated during mixing, were removed by ultrasonicating the sample for 30 min. 0.2 ml of the suspension was pipetted and spread on two microscopic glass slides (sample 1 and sample 2). In addition, a reference sample without KCl particles was prepared. All of the samples were dried at the temperature of 20^{o}C and relative humidity of 7 % (room conditions, dry winter day). The average thickness of dried varnish layer at the region of interest was measured with the optical coherence tomography (Hyperion, Thorlabs, Inc.)[11]. The optical distances were scaled with the refractive index of 1.48. The average varnish thicknesses for the samples 1, 2 and the reference were 0.67 ± 0.01 mm, 0.51 ± 0.03 mm and 0.57 ± 0.04 mm, respectively.

To evaluate the refractive index matching of drying varnish and KCl particles, a laser printed text (font size 6) on a paper was placed underneath the microscopic slides. The contrast of text was used to observe the turbidity of the varnish layer. Images of the samples were taken with two cameras; the Rikola hyperspectral camera (Rikola Ltd.) of which the filter was set at the wavelength of 590.1 nm (FWHM: 8.65 nm) and with the mobile phone camera (S7, Samsung) with the automatic lighting settings. The halogen lamp and the fluorescent lamp equipped with a yellow filter (silicone rubber colored sleeve) were used for Rikola camera and S7, respectively.

Scanning electron microscope (SEM) images of the varnish films were obtained using a field emission scanning electron microscopy (FESEM, Zeiss Sigma HD VP, Oberkochen, Germany) at 0.5 kV acceleration voltage. All samples were coated with platinum before observing. XRD analysis of samples were conducted with a Rigaku SmartLab 4.5 kW, with the equipment parameters of Co source (40 kV and 135 mA) Kα (Kα1=1.78892 Å; Kα2= 1.79278 Å; Kα1 /Kα2= 0.5), using scan rate of 3 °/min.

3. Results and discussion

3.1 Refractive index of dry varnish

The refractive index of the varnish was measured at a regulated constant (21^{o}C and 30% relative humidity) at the start (0 hour) and at the end (32 hours) of the test with the Atago RX-5000 refractometer at 589 nm, and the values were 1.4381 and 1.4834, respectively, with uncertainly of ±0.4*10-4 refractive index units. The change of refractive index of varnish in the sample container of the refractometer is shown in Fig. 1. The refractive index (i.e. drying rate) of the varnish shows a nonlinear dependence as a function of drying time. The drying process mainly consists of two different stages called as a constant rate period and a falling rate period [12,13]. In the constant rate period, the weight of coating decreases linearly with time due to the surface evaporation of solvent. At the beginning of the drying process, the paint film contains enough solvent to keep pigment particles separated. After the fast initial evaporation, the paint surface dries and the evaporation rate decreases. This period is called as the falling rate period. Since the coating layer can contain different types of solvents having a wide range of evaporation rates, the drying process becomes nonlinear as a function of time.

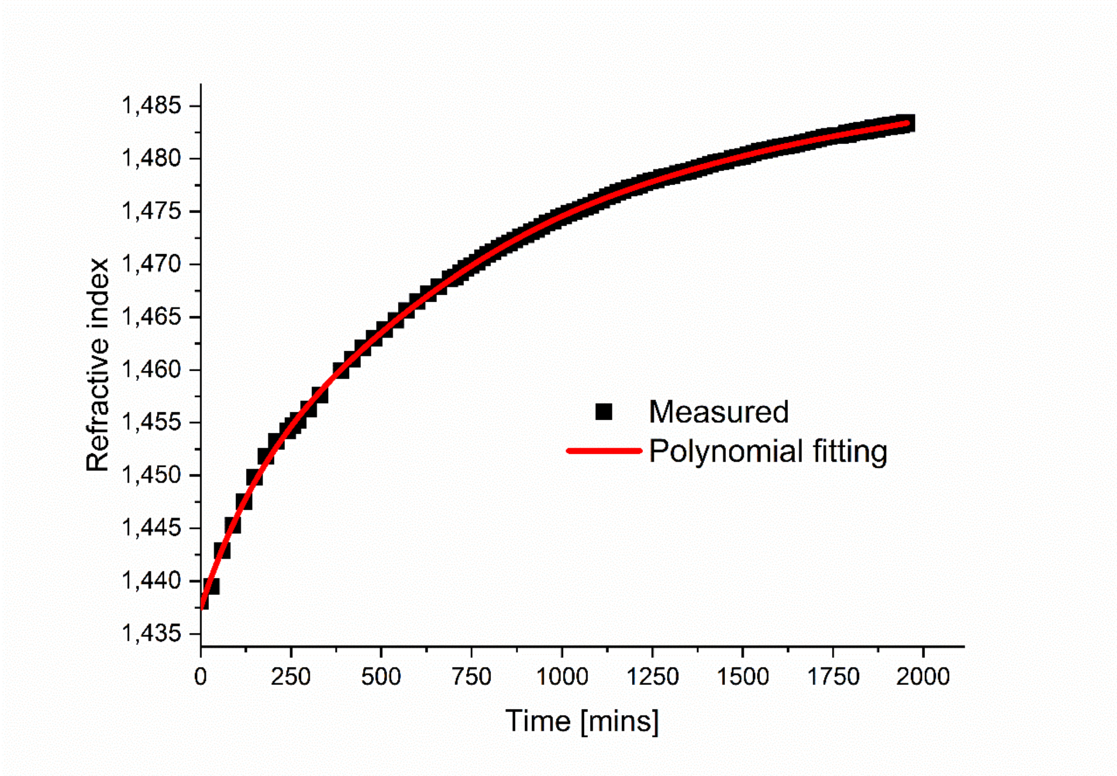

Fig.1 Refractive index of the varnish as a function of drying process time as measured by the Atago refractometer.

3.2 Turbidity evaluation of drying varnish

The wet suspension was imaged with the mobile phone and the hyperspectral camera immediately after spreading it onto the microscopic glass. For sample 1 (mobile phone), the solid KCl particles cause the varnish layer to be nearly opaque, as shown in Fig. 2a. Thus the refractive indexes of the liquid varnish and the KCl particles deviate in the beginning. As the varnish dries its refractive index approaches to that of the KCl particles. After 24 h the varnish is completely dry and underlying text becomes clearly distinguishable (Fig. 2b). When compared to the reference sample (Fig. 2c) the contrast is slightly reduced, which indicates a small residual difference in the refractive indexes.

Fig. 2. Images taken with the mobile phone Samsung S7 (automatic settings) under the fluorescent lamp equipped with a yellow filter. (a) is the varnish with the added KCl particles at the start (0 hour), (b) at the end (24 hours) and (c) is the reference sample without KCl after 24 hours of drying.

The sample 2 was imaged with the hyperspectral camera at the wavelength of 590 nm corresponding the wavelength of the Atago RX-5000 refractometer measurements. In the beginning, the varnish layer has high turbidity as shown in Fig. 3a. However, it appears to be less opaque as in the case of an image taken with a mobile phone under the yellow filtered fluorescent lamp. It is assumed that the difference is caused by the narrower bandwidth of the hyperspectral camera, which reduces light scattering at wavelengths outside the selected wavelength of 590 nm. After 3.5 hours the text becomes clearly visible (Fig. 3b), although the drying process continues. After 24 hours (Fig. 3c), the contrast is improved and became comparable to the reference sample, as can be seen in Fig. 3d.

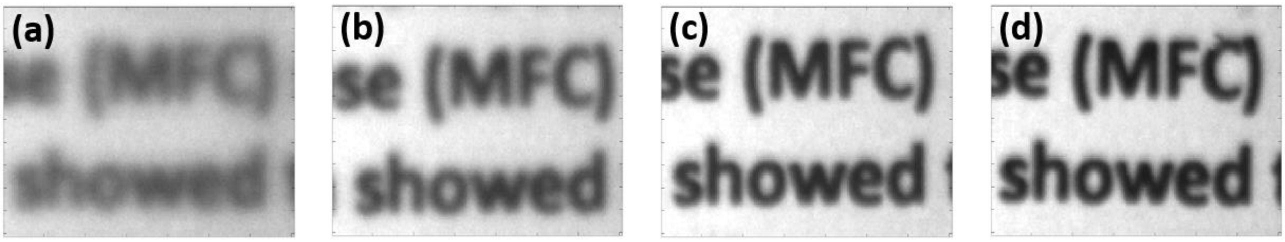

Fig. 3. Images taken with the Rikola hyperspectral camera at the wavelength of 590 nm. (a) is the varnish with the added KCl particles at the start (0 hours), (b) after 3.5 hours of drying (c) at the end (24 hours) and (d) the reference sample without KCl after 24 h of drying.

We can see from Fig. 3c and Fig. 3d that perfect transmissions could not be achieved. It could be due to light absorption in the suspension, slight birefringence of the KCl or/and refractive index difference

(Δn=0.0012) between varnish and KCl. The latter aspect can be affected by changing composition of recipe in the varnish in order to obtain a higher refractive index or to use a second particle.

3.3 FESEM images of varnish films

The FESEM images of dry films of pure varnish and varnish containing KCl are presented in Fig. 4. The reference varnish film (without any KCl) showed smooth and homogenous surface, however, some small pin holes could be observed, which were probably caused by the evaporation of the solvent when the film was drying. Compared to pure varnish film, wrinkles could be observed on the surface of KCl containing varnish sample, but no holes were found. Moreover, a number of irregular KCl particles can be observed indicating that the KCl was not dissolved in the varnish.

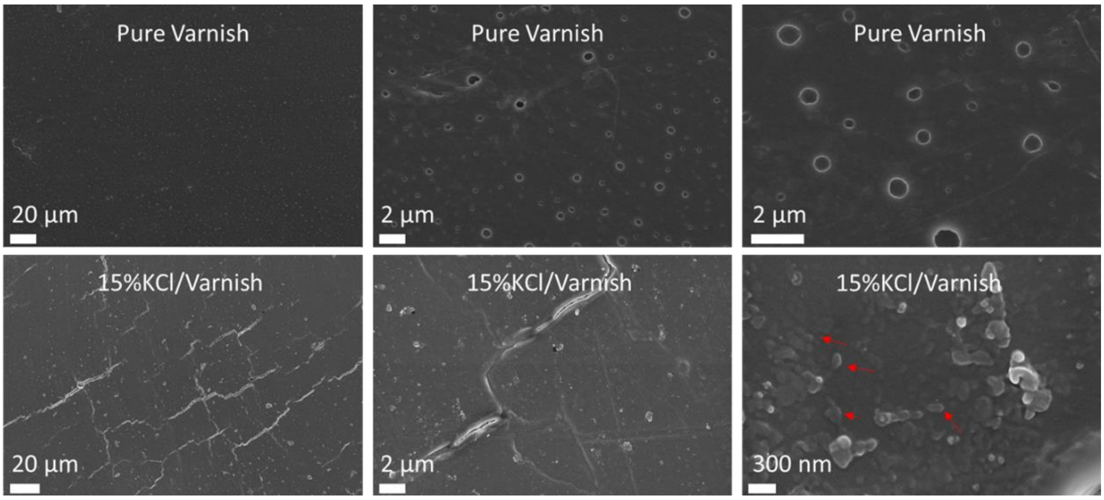

Fig. 4. Scanning electron microscopy (SEM) images of the surface of pure reference varnish and varnish film containing KCl. The red arrows points the KCl crystals.

3.4 XRD analysis of varnish films

Fig. 5 shows the XRD patterns of the pure varnish and the varnish containing 15% of KCl particles. A broad peak around 21.6° is found in the XRD pattern of pure varnish sample and the relative intensity of this peak decreased when 15% KCl was added. Moreover, typical peaks of KCl salt could be clearly observed, which shows the existence of KCl particles in the dry films and the insolubility of KCl in varnish solution.

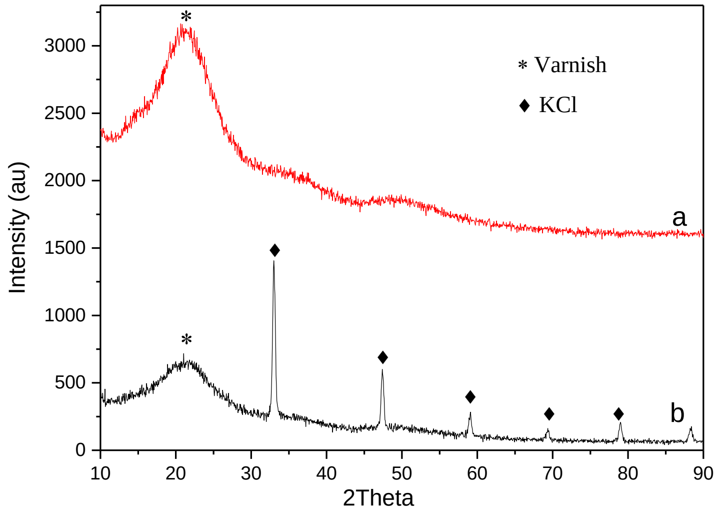

Fig. 5 XRD patterns of (a) pure Varnish and (b) 15%KCl/Varnish sample

Minimizing the needed process time (drying time in this case) is one of the key parts of optimizing the throughput of commercial processes (including coating and painting processes). By knowing exactly, when the coating is dry enough, the needed processing time can be reduced increasing the throughput eventually. Thus, this one of the most effective ways to improve the production capacity of the coating process.

We believe that particles can be homogeneously mixed in the varnishes to improve also their physical and mechanical properties. This approach allows also to design varnish composites for desired applications requiring corrosion-resistance, high mechanical strength, conductivity, anti-flammability, and thermal resistance for future industrial end-uses. In general, the particles are cheap which makes this method potentially economically feasible. In addition, the refractive index of varnish can be easily be adjusted by changing its composition or concentrations of constituents, which further broaden the applicability of the method.

4. Conclusion

We have presented a novel non-destructive and non-invasive tool to study the drying process of varnish based on immersion solid matching technique. The results indicate that the time evolution of the turbidity has strong positive correlation with drying time.

An advantage of our immersion method is that it provides information on drying of a varnish film by the relatively rapid and easy non-contact technique. Furthermore, the method does not require the use of special devices, only a mobile phone or CCD camera or just visual inspection. The challenge of the method is to find suitable material combinations (same refractive index in dry form, chemical compatibility) for coatings and added particles.

In our future plan, we continue to study how the properties of the particle can be utilized in the varnish/paint, for example, to improve thermal conductivity, corrosion, or mechanical strength.

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