Detection of Paint Curing by Non-contact Surface Resistivity Measurement

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Abstract—Commercial liquid paints are composed of pigment, resin and solvent. Paints are electrically conductive materials, because the solvent is generally a good conductor. Therefore, following the application of paint, the surface of the painted layer gradually changes from conductive to insulating due to evaporation of the conductive solvent. In this study, the degree of paint curing is monitored by non-contact surface resistivity measurement. The measurement device has a corona charger and surface potential probes. By monitoring the surface potential of the painted surface along with corona charging of the surface, the change in the surface resistivity of the painted surface can be predicted and the curing process can be quantitatively detected.

I. INTRODUCTION

Control and understanding of the painting process are very important for coating manufacturers and raw material suppliers. The control of drying times is of particular interest to achieve an economic and controllable paint coating process. A BK drying recorder is typically used by paint manufacturers to determine the characteristic drying times, such as set-to-touch, tack-free, or dry-hard times. Visual observation of the trace left by a needle drawn through the drying film at a constant speed indicates the characteristic drying times [1]. However, this method is destructive, and not applicable to actual products undergoing a painting process.

Monitoring the changes in the physical and chemical properties that occur during the paint layer curing process without destroying the paint surface is required. Recently, non-contact methods developed for the monitoring of paint drying have included the use of terahertz electromagnetic pulsed imaging [2], diffusing wave spectroscopy [3], ultrasonic reflection [4], nuclear magnetic resonance (NMR) and confocal Raman microscopy [5], and complex dielectric measurement [6]. Each of these techniques provides useful information on film formation and the drying process. However, most of them are not capable of measuring the build-up of properties under realistic conditions of solvent evaporation.
and/or on an appropriate substrate. In addition, these techniques require know-how and substantial analysis time. Thus, a simple technique that allows real time monitoring using a low cost sensor is necessary for application to manufacturing processes.

We have developed a non-contact technique to measure the surface resistivity of a coated layer on an insulating material [7-9]. The surface resistivity of the paint layer increases and the layer changes from conductor to insulator as the conductive solvent evaporates during the drying process. Therefore, monitoring of surface resistivity can be an alternative method for the evaluation of paint drying or curing. In this investigation, the surface resistivity of a paint layer is correlated with the degree of curing.

II. EXPERIMENTAL SETUP

A. Electrodes for Non-contact surface resistivity measurement

Figure 1 shows a schematic diagram of a cylindrical grounded electrode with a corona charger used for the experiment. The radius and length of the grounded cylinder are 10 and 160 mm, respectively. A corona charging electrode is inserted at the center of the grounded cylinder and is composed of a high voltage needle electrode and a grounded ring electrode with an inner diameter of 4 mm. The tip of the needle electrode penetrates the center of the ring electrode at a distance of 3 mm, so that the tip of the needle electrode is located at the bottom of the grounded cylindrical electrode. Two surface potential probes (#1 and #2) are embedded in the bottom of the cylinder and are placed at equal distances from the needle electrode (Xc = 35 mm). The sensitivity of surface potential probe #2 is 40 times larger than that of probe #1 to measure low potential.

A painted test material is placed below the grounded cylindrical electrode at a gap, δ, of 1 mm. When a dc high voltage is applied to the needle electrode, corona discharge occurs between the tip of the needle and the grounded ring electrode. Some of the corona ions arrive on the painted test material and the surface potential becomes $V_0$ just below the needle. An electrical circuit is formed between the grounded cylinder and the charged test

Fig. 1. Experimental setup
material, so that the surface potential distribution around the charged spot can be predicted by [9]:

\[
\frac{v}{V_0} = \exp\left(-\frac{\rho_s}{\sqrt{\rho_s \cdot \delta} \cdot X_c}\right),
\]

(1)

where \(v\) is the saturated surface potential measured at a distance \(Xc\) from the center of the charged spot, \(V_0\) is the surface potential at the center of the charged spot, \(\rho_s\) is the surface resistivity of the painted layer, \(\delta\) is the air gap between the grounded cylinder and the painted layer, and \(\rho_s\) is the volume resistivity of the air gap \((4 \times 10^{13} \, \Omega \cdot \text{m})\) [10]. The term \(v/V_0\) is the normalized surface potential and is a function of the surface resistivity, because \(\delta\), \(\rho_s\), and \(Xc\) are constant values. The two probes are located the same distance from the needle electrode; therefore, \(v/V_0\) measured at the two probes should be the same.

Figure 2 shows the relationship between the surface resistivity and the normalized surface potential for \(Xc = 35\, \text{mm}\) and \(\delta = 1\, \text{mm}\) calculated using Eq. (1). A significant change in the normalized surface potential is observed for a surface resistivity greater than \(10^9\, \Omega/\square\), which indicates that the measurable range is not in the conductive region, but is dissipative to insulative. This measurable range should be suitable to monitor paint curing, because most of the conductive solvent is evaporated at the set-to-touch, tack-free, or dry-hard states to be evaluated. The system is not experimentally calibrated as a surface resistivity tester, so that the normalized surface potential can be directly used as an indicator of the curing state.

**B. Preparing test samples and measurements**

Commercial solvent based paint A (silver metallic) and water based paint B (blue) were used as test paints. A 2 mm thick plastic plate was painted with paint A using a spray gun to a thickness of approximately 30 \(\mu\text{m}\). Painted layers of paint B were formed using an edge
coater (TC-1, Mitsui Denki Seiki Co., Ltd.) with thicknesses of 30 and 70 µm. The painted plastic plate was placed below the electrode with a gap, δ, of 1 mm. A dc high voltage of +3.5 kV was applied to the needle electrode, and the surface potential was immediately increased and saturated. At the fresh paint stage, the paint layer was conductive with equipotential. The measured surface potential is the same as potential $V_0$ just below the needle; therefore, $V_0$ can be measured from the potential below probe #1 just after the painting operation.

The saturated surface potential was measured for different exposure times $T_e$, and the normalized surface potential $v/V_0$, was calculated. The saturated potential $v$ was defined by the potential measured at 60 s after high voltage application to the needle electrode. The painted surface was charged up due to corona charging; therefore, the surface was neutralized using an ionizer after each measurement. The room temperature was 15-18 °C and the relative humidity was 34-58% during the experimental measurements.

C. Measurement of paint layer hardness

To characterize the curing state of the paint layer, the hardness of the layer was measured by pencil hardness, which is the standard for film hardness (ASTM D3363). At first, a 6B pencil was selected and a line of approximately 2.5 cm was made on the painted layer using the tester shown in Fig. 3. If the pencil did not leave a scratch, then a harder pencil was used when the procedure was repeated. The first pencil that leaves a scratch on the paint layer is considered as the pencil hardness of layer. The tester applies a weight of 750 g to the pencil, which is held at an angle of 45°. The pencil hardness was measured at different exposure times $T_e$, in addition to the normalized surface potential measurements.

Fig. 3. Pencil hardness tester.
III. RESULTS & DISCUSSION

A. Time dependence of normalized surface potential

1) Solvent-based paint A

Figure 4(a) shows the time variation of the normalized surface potential for paint A. The normalized surface potential just after paint application was 1, because the paint layer was regarded as a conductor due to the high content of conductive solvent in the paint layer. The surface potential was decreased to 0.1 at $T_e$ of 2 min. Paint A includes an organic solvent with a faster rate of evaporation, so that the surface potential is rapidly decreased, and the conductive paint layer become insulative, in a short period of time. In this case, application of voltage to the needle was maintained for 5 min. The observed potential drop was caused by elimination of the surface charge due to evaporation of the solvent at the surface of the paint layer, and the surface resistivity become significantly high value. Because the surface charge below the needle electrode can not move to the measuring spot, the surface potential of the measuring spot is not increased. The variation of the normalized surface potential with time indicates the solvent evaporation rate from the paint layer.

2) Water-based paint B

Figure 4(b) shows the normalized surface potential for a paint thickness of 30 µm. The normalized surface potential is gradually decreased, in contrast to the solvent based paint A (Fig. 4(a)). The normalized surface potential remained high at over 0.8 for 5 min and then gradually decreased to less than 0.1 after 15 min. The slow potential drop is due to the slow evaporation rate of the water solvent from the paint. In this case, there was no charge elimination during the application of the voltage. The surface potential increased with time and the saturated voltage $v$, was measured at 60 s after voltage application. After the measurement, the test surface was neutralized using the ionizer. If the surface was kept charged after the measurement, then the electrostatic attractive force between the grounded cylinder and the charged surface would slowly deform the surface. However, there was no
deformation of the paint surface during the 60 s surface potential measurement.

Figure 5 shows a comparison of the normalized surface potential of paint B for different initial thicknesses of 30 and 70 μm. During the early stage after paint application, the normalized surface potential remained constant at approximately 1, regardless of the paint thickness. Figure 2 shows that the normalized surface potential of a conductive surface with a surface resistivity less than $10^9$ Ω was 1, regardless of the surface resistivity. Therefore, the measurement system had no sensitivity in this range. The normalized surface potential of the 70 μm thick layer remained constant at approximately 1 for a longer period than the 30 μm thick layer, which indicates that the thicker paint layer requires a longer time for evaporation of the conductive solvent.

As the normalized surface potential dropped to 0.3-0.4, the top surface of the painted layer was dried to the set-to-touch state for both samples. From observation, the painted surface became tack-free at 150 min after paint application. The sensitivity to a normalized surface potential less than 0.1 is not very high using surface potential probe #1; therefore, the higher sensitivity surface potential probe #2 was used to measure lower surface potentials. Figure 6 shows the normalized surface potential of a 70 μm thick layer of paint B measured using the combination of the two probes. The normalized surface potential started to drop at 45 min after paint application and became saturated at 0.002 after 3 h. The normalized surface potential of 0.002 was the minimum limit of the measurement. The tack-free state was observed when the normalized surface potential was 0.007. The dry-hard state could not be measured from the normalized surface potential with this system due to the minimum limit of the surface potential measurement.

Fig. 5. Variation of the normalized surface potential as a function of exposure time for 30 and 70 μm thick paint B layers.
B. Degree of curing

The normalized surface potential indicates the degree of curing, $D_c$. To monitor paint curing, an indicator of the degree of curing is proposed using Eq. (2) with the normalized surface potential.

$$D_c = \ln \left( \frac{v}{V_0} \right)^{-1} \quad (2)$$

$D_c$ is defined by the logarithm of the inverse normalized surface potential. The inverse of the normalized surface potential is used to obtain higher values as the curing stage proceeds. The logarithm of the value is taken to realize a smaller dynamic range for the indicator. For wet and conductive surfaces, $D_c = 0$, because the normalized surface potential is 1. For dry-hard and insulative surfaces, $D_c = 6$, because the minimum normalized surface potential is 0.002. Thus, the degree of curing is represented by values from 0 to 6, where the higher value indicates a harder surface.

Figure 7 shows a comparison of the variation of $D_c$ with time, as calculated from Fig. 6 (line) and that measured using pencil hardness (plots). $D_c$ is zero when the surface is wet and conductive, then begins to increase at $T_e = 45$ min. When $D_c = 1$, the pencil hardness is measured as 6B and the surface is regarded to be at the set-to-touch stage. When $D_c = 5$, the pencil hardness is measured as B and the surface is regarded to be at the tack-free stage. Thus, the set-to-touch and tack-free times were indicated by $D_c$ at 1 and 5, respectively. The dry-hard time could not be measured, because $D_c$ is over the range when the pencil hardness is measured as HB. However, the $D_c$ profile is in approximate agreement with the measured pencil hardness. The pencil hardness at the dry-hard stage is dependent on the material properties of the resin or pigment in the paint. If a relationship between $D_c$ and the pencil hardness is established for the paint of interest by preliminary experiment, then the curing...
Although $D_c$ relates to the curing state (Fig. 7), it also relates to the surface resistivity derived using Eq. (1):

$$D_c = \ln \left( \frac{v}{V_0} \right)^{-1} = \sqrt{\frac{D_z}{\rho_x \delta}} \cdot X_c. \quad (3)$$

The right hand side of Eq. (3) represents a non-dimensional value that represents the ratio of the surface resistivity of the paint layer to the volume resistivity of air. Therefore, the hardness of the paint layer is related to the electrostatic properties, including the surface resistivity of the paint layer, because both the surface resistivity and hardness are a function of the conducting solvent content in the paint layer.

Further investigations are required to understand the detailed relationship between the surface resistivity and the paint curing state using different types of paints.

**References**


