STRUCTURE FORMATION DURING DRYING OF COATING LAYER OF MAGNETIC PARTICULATE CONTAINING SOLVENT MIXTURE

HAIIME TAMON*1, KENJI TAKASE, HIDENORI TANAKA, HIROKI MIURA*2 AND MORIO OKAZAKI
Department of Chemical Engineering, Kyoto University, Kyoto 606-01

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It is important to understand the structure formation during drying of coating layers of magnetic particulate from the viewpoint of design of dryers and better quality of magnetic recording media. Drying characteristics of coating layers containing cyclohexanone and toluene were measured, and the change of intensity of reflected light at the layer surface was determined during drying. Then, surface and inside characteristics of dry layers were evaluated by gloss measurement and nitrogen adsorption. If the initial mass fraction of toluene was less than 50 wt% in the solvent mixture, toluene shortened the drying time and did not influence the gloss and the pore volume of dry layers. The influence of drying conditions on surface and inside characteristics of dry layers was qualitatively explained based on the model previously proposed by the authors.

Introduction

The quality of coated web often depends on the structure of the coating layer. It is very important to understand the structure formation of the coating layer. For example, in magnetic recording media such as floppy disks and audio tapes, the surface structure plays an important role in recording characteristics, and the bulk needs adequate voids to preserve lubricant that should come out to the film surface gradually to protect it from friction damage. Thus, it is necessary to understand the structure formation during drying in order to improve the product quality or to design the dryer for the recording media.

The drying mechanism of polymer films has been well studied and mathematical models have been proposed by taking into account diffusion and volumetric shrinkage within the materials. Some attempts have been made to study the quality of dry coating films. Braun has elucidated the contribution of pigments to the gloss of paint films. Lepoutre and Rigdahl have reported the effect of pigment shape on the stiffness of coatings. Binder migration is also important during drying of coatings. Krishnapalan and Simard have studied binder migration in coated papers by use of an electron microprobe, and elucidated that the distribution of binder depends on drying rates. Kline has studied the binder migration tendency by combining a controlled drying method and ultraviolet surface analysis.

We have measured drying characteristics of the coating layer of magnetic particulate and observed the structure of the dry layer by use of an electron microscope (SEM) and gloss measurements. We have proposed a model for structure formation of the coating layer, and qualitatively explained the influence of drying conditions on the surface or inside structure of the layer based on the model. We have also elucidated the origin of inside void structure of coating layers by use of a nitrogen adsorption method. However, the structure formation of the coating layer of magnetic particulate has not been studied in cases where the layer containing solvent mixture is dried.

In this article, we study the structure formation during drying of the coating layer of magnetic particulate, which contains two kinds of solvents. We measure the change of solvent content, surface temperature and intensity of reflected light at the surface during drying, and determine surface and inside characteristics of the dry layer by use of nitrogen adsorption and gloss measurement. We also try to explain the solvent effect on the structure formation of the coating layer based on the previously proposed model.

1. Experimental

1.1 Preparation of paint

Paints usually consist of one kind of pigment, several kinds of binders and solvents, a dispersing agent, lubricant, and so on. However, our model paint contains only four components so we can understand the drying process easily. Table 1 shows the components of standard model paints used in this work. Vinyl chloride copolymer with a sulfonyl group acts not only as a binder, but also as a dispersing agent of the pigments. Cyclohexanone and

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*1) Correspondence concerning this article should be addressed to H. Tamon.
*2) H. Miura is with Kao Corp., Tochigi 321-34.
Table 1 Composition of model paint

<table>
<thead>
<tr>
<th>Paint</th>
<th>No. 1</th>
<th>No. 2</th>
<th>No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigment</td>
<td>28.0 wt%</td>
<td>28.0 wt%</td>
<td>28.0 wt%</td>
</tr>
<tr>
<td>Binder</td>
<td>7.0 wt%</td>
<td>7.0 wt%</td>
<td>7.0 wt%</td>
</tr>
<tr>
<td>Solvent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>65.0 wt%</td>
<td>32.5 wt%</td>
<td>13.0 wt%</td>
</tr>
<tr>
<td>toluene</td>
<td>0.0 wt%</td>
<td>32.5 wt%</td>
<td>52.0 wt%</td>
</tr>
</tbody>
</table>

pigment: Co - 7: Fe$_2$O$_3$ (needle-like pigment, long axis: 0.3 μm, short axis: 0.03 μm); binder: vinyl chloride copolymer

toluene were used as solvents in this work.

In the preparation of paints, the binder polymer was first dissolved into the solvent mixture. Then, pigments were dispersed in the binder solution by use of a ball mill. A well-dispersed paint results in a smooth surface after drying. From gloss measurements of the dry coating layers, a milking time of 40 hours was chosen according to the previous work$^9$.

1.2 Drying Experiment

We prepared coated films by use of an applicator of 100 μm gap width. The paint was applied to a polyethylene terephthalate (PET) film substrate of 75 μm thickness. Then, the coated film was cut to the proper size (12 cm × 8 cm) and placed on the sample stage in a hot air dryer. Solvent loss of the film during drying was about 450 mg. The temperature of hot air was 40°C, 60°C or 80°C, and the velocity of the air was 1, 3 or 5 m/s. The experimental apparatus and the detailed procedure of drying experiments have been described in the literature$^{10}$.

In situ measurements for solvent content, surface temperature and reflected light at the surface were conducted during drying. The mass change of films was measured with an electronic balance (Mettler: PFP300) with 1 mg accuracy. The surface temperature of the coatings was measured with an infrared thermometer (Keyence: IT2-50) and the intensity of reflected light at the surface of the coatings was determined by an optical fiber probe (OMRON: E32-D51).

1.3 Evaluation of dry coating layer

The structures of the coating layers dried under various conditions were evaluated in terms of pore-size distribution and gloss.

We determined the pore volume and the pore-size distribution by N$_2$ adsorption at 77 K. A nitrogen adsorption apparatus (Japan Bell; BELSORP22) was used for this measurement. The pore-size distribution was calculated from the desorption isotherm by use of the method proposed by Dollimore and Heal$^3$. The standard isotherm of N$_2$ on FeOOH was used to calculate the adsorption layer thickness.

The intensity of reflected light depends on the angle of observation, the refractive index of surface and the surface roughness$^6$. The gloss is defined as the ratio of the intensity of reflected light to the intensity of incident light. The gloss of dry layers was measured with a glossmeter (Suga: UGV-5D). The angles of incident light and observation were set to 60° in this work. We used gloss as a measure of the smoothness of the layer surface.

(a) Surface evaporation period

(b) Critical point

(c) Falling rate period

Fig. 1 Schematic illustration of structure formation during drying

2. Results and Discussion

2.1 Drying model of structure formation

We have proposed a drying model for the structure formation of coating layers as shown in Fig. 1$^9$. The first period of drying before the critical point is shown in Fig. 1 (a). The layer shrinks due to the loss of solvent, and the amount of shrinkage is equal to that of solvent evaporated. The pigments gradually adopt more horizontal orientation. The surface of the coating layer is flat because the surface tension is larger than the yield stress of the coatings$^9$. Figure 1 (b) shows a schematic feature at the critical point. At the critical point when the yield stress of the layer exceeds the surface tension, the layer surface begins to roughen. The drying front recedes into the layer and voids are formed after the critical point as shown in Fig. 1 (c). We suppose that the void characteristics depend on the surface tension at the drying front and the drying rate.

When the surface tension is large, the critical solvent content is small compared with the case of small surface tension$^9$. If the binder solidifies before the layer surface begins to roughen, the pigments adopt horizontal orientation. On the other hand, in cases where the surface tension is small, the layer surface begins to roughen in the region of small yield stress (large solvent content). The binder solidifies after the surface roughens. Thus, pigments deviate from the horizontal orientation.
2.2 Change of surface characteristics during drying

The change of solvent content $w$, surface temperature of coatings $Ts$ and reflected light at the surface $I_r$ were measured. Figures 2, 3 and 4 show some examples. The initial thickness of the coating layer was 100 µm, and the layer was dried at 40 °C and 1 m/s. The mass ratio of toluene to cyclohexanone $\alpha$ was 0, 1 or 4 as shown in Table 1. As seen from these figures, a large value of $\alpha$ brings a high drying rate, because the boiling point of toluene (110.6 °C) is lower than that of cyclohexanone (155.7 °C). When toluene is mixed with cyclohexanone, the drying rate becomes large and the drying time becomes short. However, we should elucidate the influence of toluene on the quality of coating layer.

1) Drying of coating layer of No. 1 paint Figure 2 shows that $w$ decreases almost linearly, and that $I_r$ increases in the surface evaporation period from 0 to about 150 seconds. After about 150 seconds, $I_r$ starts dropping, and $Ts$ begins to rise sharply. $I_r$ remains constant after 200 seconds.

We can explain the change of $I_r$ based on Fig. 1. $I_r$ increases with the refractive index of surface and decreases with the surface roughness. Since the refractive index of pigments is much larger than that of binder or solvent, the index increases with the concentration of pigments. In the surface evaporation period, the concentration of pigments increases and the refractive index also increases as the coating layer is dried. In this period, the layer surface remains smooth because the surface tension is larger than the yield stress of the layer surface. Hence, $I_r$ increases as the coating layer is dried.

When the growing yield stress of the layer exceeds the surface tension, the surface can not remain smooth. After the critical point, $I_r$ greatly decreases. $I_r$ remains constant after 200 seconds because the surface structure has been fixed already. However, one can see that drying continues after 200 seconds. The result suggests that the drying front recedes into the coating layer in the period where the rate falls.

2) Drying of coating layer of No. 2 paint As seen from Fig. 3, the drying rate is not constant, even in the surface evaporation period. This figure also shows two peaks in the change of $I_r$.

$I_r$ increases with the concentration of pigments. When the yield stress of the layer surface exceeds the surface tension, the surface begins to roughen and $I_r$ decreases. Toluene easily evaporated compared with cyclohexanone because of its low boiling point. The surface tension of cyclohexanone (0.0351 N/m at 15 °C) is larger than that of toluene (0.0290 N/m at 15 °C). Hence, the surface tension of solvent mixture increases as the layer is dried, and the surface recovers its smoothness. When the yield stress of coating layer is larger than the surface tension, $I_r$ decreases again. $I_r$ becomes constant after the surface structure is fixed. In this case, only cyclohexanone influences the surface structure of the coating layer, as it did in the case of No. 1 paint.

3) Drying of coating layer of No. 3 paint One can see only one peak of $I_r$ just after the start of drying as shown in Fig. 4. Since the initial cyclohexanone content is small, its residual amount is very small at the critical point. Hence, toluene influences the surface structure of coating layer.

We have discussed the surface structure formation of the coating layer based on the difference between the surface tensions of cyclohexanone and toluene. It is well known that the binder migrates to the surface and concentrates there during drying of the coating layer. Although the surface tension may be influenced by the concentrated binder, we believe that binder migration does not influence so much as the surface tension of toluene becomes larger than that of cyclohexanone. However, a detailed study on binder migration during drying of the layer will be needed.
in the future to simulate the structure formation of coatings quantitatively.

2.3 Surface characteristics of dry coating layer

Figure 5 shows the relation of gloss $\eta$ and maximum drying rate $R_{max}$. One can see that $\eta$ for $\alpha = 1$ is almost equal to that for $\alpha = 0$ from Fig. 5. As described above, almost all toluene evaporates before the surface structure is formed. Hence, toluene does not influence the surface structure in case of $\alpha = 1$. On the other hand, the gloss for $\alpha = 4$ is much smaller than that for $\alpha = 0$ or 1. The surface is considered to roughen because the initial toluene content is large and the surface tension decreases at the critical point. The experimental results suggest that gloss depends on the toluene content rather than the drying conditions.

2.4 Void characteristics of dry coating layer

Figure 6 shows pore-size distributions for coating layers dried at 80 °C and the packed bed of magnetic particulate. As seen from Fig. 6, the coating layers with pigment have similar voids to the packed bed of pigment particulate. The peak of pore-size distribution lies at around 30 nm. These results suggest that the inside void structure of the coating layers is attributed to the packing of magnetic particulate within the layer in the case of solvent mixture.

The relation of the pore volume $V_p$ for $r < 100$ nm and the maximum drying rate $R_{max}$ is shown in Fig. 7. This figure shows very interesting results. In the drying of the coating layer of No. 1 or 2 paint, $V_p$ increases with $R_{max}$. On the other hand, $V_p$ decreases with $R_{max}$ in the drying of the coating layer of No. 3 paint.

In the case of No. 1 paint, the large drying rate results in higher porosity of the coating layer. When the coating layer is dried slowly, the pigments adopt horizontal orientation and the packing of pigments becomes denser. During rapid drying, on the other hand, toluene evaporates rapidly and the binder solidifies before horizontal orientation. Hence, the packing becomes looser. This qualitatively explains why faster drying results in a rough surface and higher porosity as shown by $\alpha = 0$ in Figs. 5 and 7.

In the drying of the coating layer of No. 2 paint, toluene is supposed to evaporate before the structure is formed, and the inside structure formation can be explained as in the case of No. 1 paint.

For No. 3 paint, if the drying rate is fast, the residual ratio of cyclohexanone is large when the inside structure is fixed. The pigments adopt horizontal orientation because of the large surface tension of cyclohexanone. Hence, the packing of pigments becomes denser, and $V_p$ is small. When the coating layer is dried slowly, the residual toluene content is great at the formation of inside structure of the layer. Hence, the drying front within the coating becomes rough, and the packing of pigments results in a large pore volume.

As shown in Fig. 7, $V_p$ for No. 3 paint ($\alpha = 4$) is larger than that for No. 1 paint ($\alpha = 0$) or No. 2 paint ($\alpha = 1$) when the layer is slowly dried. Since the content of toluene for No. 3 paint is large and the surface tension is small, the structure of drying front within the layer roughens and the packing of pigments becomes looser. This loose packing means the large pore volume of coatings.
Contrary to our expectations, Fig. 7 shows that $V_p$ for No. 3 paint is smaller than that for No. 1 or 2 paint if the drying rate is fast. In the present stage of investigation, we suppose that binder migration influences the inside void characteristics in the case of high toluene content. If we assume that much binder migrates from the inside to the layer surface in the surface evaporation period, less binder remains in the bulk than at the surface. Hence, we suppose that the pigments rearrange and the packing becomes denser before the inside structure is fixed by solidification of the binder. However detailed study on binder migration during drying will be needed in the future to verify our hypothesis experimentally.

Conclusion

The structure formation of the coating layer of magnetic particulate was experimentally studied in the drying of the layer, which contains cyclohexanone and toluene. In situ measurements of solvent content, surface temperature and intensity of reflected light at the surface were conducted during drying. Surface and inside characteristics of coating layers were evaluated by gloss measurement and nitrogen adsorption. The following conclusions were obtained from the experimental results.

1) If the initial mass fraction of toluene is less than 50 wt%, toluene does not influence the gloss and the pore volume of dry coating layers.

2) If the initial fraction of toluene is 80 wt %, the gloss of the dry coating layer is greatly decreased, and the pore volume decreases with the drying rate.

3) It is suggested that there is an optimum composition of solvent mixture to shorten the drying time and to maintain the quality of coating layers.

4) The influence of drying conditions on surface and inside characteristics of coating layers is qualitatively explained by the model previously proposed by the authors.

Nomenclature

- $I_r$ = intensity of reflected light [mV]
- $R_{max}$ = maximum drying rate [kg m$^{-2}$ s$^{-1}$]
- $r$ = pore radius [nm]
- $T_s$ = surface temperature of coating layer [$^\circ$C]
- $t$ = time [s]
- $V_p$ = pore volume [m$^3$/kg]
- $w$ = solvent content [kg/kg]
- $\alpha$ = mass ratio of toluene to cyclohexanone [-]
- $\eta$ = gloss of surface [-]

Literature Cited

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