

Effect of White Pigments on UV Curing of Inks

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Synopsis

The dynamic viscosity of ultraviolet (UV) inks during curing was measured by the use of an oscillating plate rheometer and the cure rate was determined rheologically. The effect of white pigments on the cure rate is discussed in relation to absorption and scattering of UV radiation by the pigments. In white inks, the scattering, which depends primarily on the difference in refractive index between the pigment and the vehicle, has an important role in controlling the cure rate. A pigment with a refractive index very close to that of the vehicle has little adverse effect on the cure rate. Thin films of ink containing a pigment with a high refractive index are rapidly cured because of the increase in optical path length by scattering. However, the cure rate is greatly reduced when the thickness is increased due to the rapid decay of UV radiation with depth in the film. The absorption of UV radiation by the photoinitiator in a film which absorbs and scatters radiation is calculated, from which the cure rate is predicted. The theoretical prediction shows good agreement with the experimental results.

INTRODUCTION

Ultraviolet (UV) is widely used as a method of curing clear coating and pigmented inks. The curing of such systems requires the absorption of UV radiation by a photoinitiator which, in turn, generates free radicals to initiate polymerization. To cure the film completely, UV radiation must reach the bottom of the film and be absorbed as well as in the upper layer of the film. One of the problems in curing the film containing a pigment is rapid attenuation of the incident light by the pigment. Two physical phenomena are responsible for the attenuation of UV radiation by pigments in ink films: absorption and scattering.

Absorption by the pigment in a colored ink is very strong and not involved in the photochemical reaction. The presence of a highly absorbing pigment such as carbon black drastically reduces the radiation absorption by the photoinitiator and thus the thickness of film which can be cured. An important role of opaque coatings is to cover or hide the substrate. The hiding power of a pigment is determined by its ability to absorb and scatter visible radiation. In the case of white pigments, hiding is accomplished by scattering, which depends primarily on the difference in refractive index between the pigment and the medium (vehicle). The effect of scattering of UV radiation on the cure rate of film is very complicated. Theoretical prediction¹ implies that in a thin film with a high scattering coefficient even more radiation is absorbed by the photoinitiator than in the absence of pigment, because of the increase in optical length of radiation passing through the film. Thin films of

white inks at low pigment concentrations can be cured more rapidly than the vehicle, but the cure rate of thick film is greatly reduced because of the decrease in penetration depth of UV radiation. In practice, to give appropriate rheological properties, extender pigments are often used, which have refractive indices very near to those of vehicles (about 1.5) and absorb little visible light. Since the degree of scattering by the extender pigments is considerably low, they have little adverse effect on the cure rate. In general, the attenuation of UV radiation varies depending not only on type, particle size, and concentration of pigment, but also on wavelength of the light used to cure the film. It is essential to understand the cure rate of UV inks in relation to the absorption and scattering of UV radiation by the pigments.

In previous papers,²⁻⁴ we have measured the dynamic viscosity of four colored inks (cyan, magenta, yellow, and black) during UV curing by the use of an oscillating plate rheometer. The rheologically determined cure rate was explained on the basis of the competitive absorption between photoinitiator and pigment at the bottom of the film. In the present study, the rheology of UV inks containing white pigments was measured during curing under a monochromatic light of 365 nm. The effect of pigments on the curability is discussed in terms of absorption coefficient and refractive index of the pigments.

EXPERIMENTAL

Samples

The vehicle was formulated using 54 wt% epoxy acrylate prepolymer (Epicon 1050 from Dainippon Ink & Chemicals Corp.), 36 wt% trimethylol propane triacrylate (TMPTA), and 10 wt% photoinitiator. The photoinitiator was 2,2-dimethoxy-2-phenylacetophenone. The vehicle is sensitive to wavelengths of 297, 302, 313, 334, and 365 nm.

The pigments used were rutile titanium dioxide, zinc oxide, and barium sulfate, the typical properties of which are shown in Table 1. Ultraviolet inks were prepared at concentrations up to 40% by weight.

Apparatus

The apparatus was an oscillating plate rheometer in which the sample was sheared between a fixed plate and an oscillating plate made of a quartz glass. The details of apparatus and the method of measurement have been reported elsewhere.^{5,6} The time dependence of dynamic viscosity during UV curing was

TABLE 1
Typical Properties of Pigments

	BaSO ₄	TiO ₂	ZnO
Diameter (μm)	< 0.2	0.3	< 0.2
Density (g · cm ⁻³)	4.5	4.2	5.6
Refractive index (-)	1.63	2.76	2.0

measured at various sample thicknesses in the range of 5–40 μm . Since the initial dynamic viscosity η'_0 (before UV radiation) varied with type of pigment and concentration, the relative viscosity η'/η'_0 is used to characterize the progress of curing reaction. The frequency was held at 80 Hz and the temperature at 30°C.

The UV source was a high-pressure mercury lamp, the spectral output of which had sharp peaks at various wavelengths. Since the 365 nm absorption is of primary importance, a UV filter with a 350 nm cutoff was used. The total light intensity was 27 $\text{mW} \cdot \text{cm}^{-2}$ at the surface of filter. Our attention is focused mainly on the rheological behavior during UV curing induced by a monochromatic light of 365 nm.

RESULTS

Figure 1 shows the effect of sample thickness on the viscosity change of vehicle during UV curing. The abscissa (exposure energy) is defined as the product of exposure time and the light intensity at the upper surface of UV filter. The relative viscosity begins to increase beyond a certain exposure energy and then linearly increases with exposure energy. Because the data can be approximated by two straight lines, the exposure energy at the intersection between two lines is used as a measure for UV curability. This is referred to as the minimum exposure energy E_m in this study. The minimum exposure energy shows a little increase with sample thickness.

Figure 2 shows the effect of sample thickness on the viscosity change of ink containing 40 wt% BaSO_4 during UV curing. The curing behavior is almost the same as the vehicle, except that the addition of BaSO_4 causes the minimum exposure energy to decrease very slightly. The inks containing lower concentrations of BaSO_4 are rapidly cured as well as the vehicle. If pigment particles that absorb no visible light are dispersed in a vehicle whose refractive index is the same as the pigment, the ink may be clear. BaSO_4 is very useful as an extender pigment because its refractive index is very close to that of vehicle (1.5 ~ 1.6). White pigments with refractive indices of 1.5 ~ 1.6 may have little adverse effect on the curing rate.

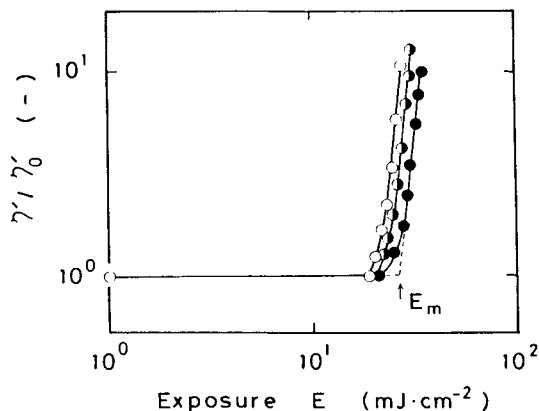


Fig. 1. Dependence of relative viscosity on the exposure energy at different film thicknesses for vehicle during UV curing: (○) 6.1 ; (◐) 18.3 ; (●) 30.1 μm .

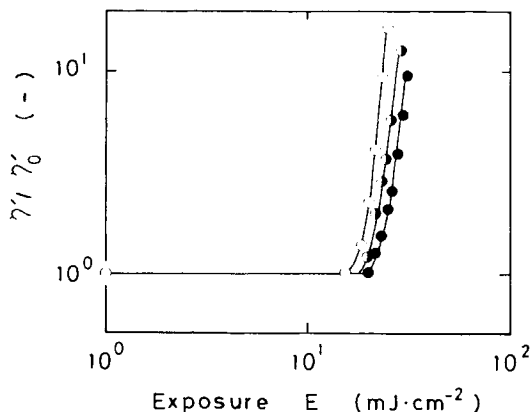


Fig. 2. Dependence of relative viscosity on the exposure energy at different film thicknesses for 40 wt% BaSO₄ ink during UV curing: (○) 6.2; (⊙) 20.1; (●) 30.0 μm.

Figures 3 and 4 show the curing behavior of 5 wt% TiO₂ ink and 10 wt% TiO₂ ink, respectively. Although a thin film for both inks gives a cure rate comparable to the vehicle, it is markedly reduced as the film thickness increases. This tendency is more remarkable for 10 wt% ink. For instance, the minimum exposure energy at 20 μm for 10 wt% ink is about 10 times larger than that for the vehicle. Moreover, the slope of the line decreases with increasing sample thickness, whereas that for the vehicle is constant irrespective of thickness. In a practical sense, the film thickness that can be effectively cured by a given UV lamp drastically decreases with increasing TiO₂ concentration and film thickness.

Figures 5 and 6 show the curing behavior of 5 wt% ZnO ink and 10 wt% ZnO ink, respectively. Apparently ZnO reduces the curability of ink in a similar way as does TiO₂. It is of interest to note that for films with thickness less than 20 μm, the slope of curve beyond the minimum exposure energy is independent of type of pigment, concentration, and film thickness. Pappas

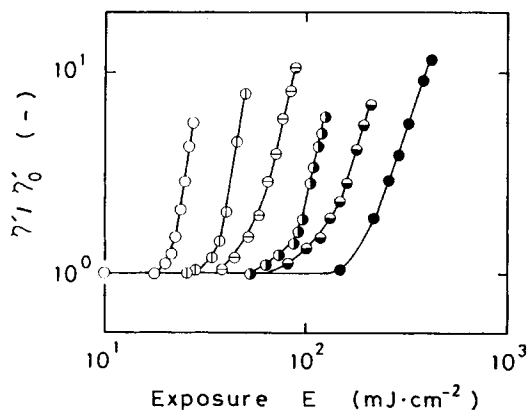


Fig. 3. Dependence of relative viscosity on the exposure energy at different film thicknesses for 5 wt% TiO₂ ink during UV curing: (○) 6.1; (⊙) 11.0; (⊖) 17.4; (●) 20.7; (⊙) 25.8; (●) 30.8 μm.

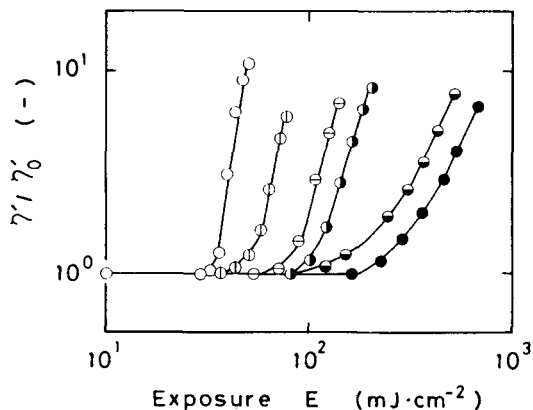


Fig. 4. Dependence of relative viscosity on the exposure energy at different film thicknesses for 10 wt% TiO_2 ink during UV curing: (○) 6.1 ; (◻) 9.2 ; (◻) 12.2 ; (●) 14.3 ; (◐) 18.3 (●) 22.2 μm .

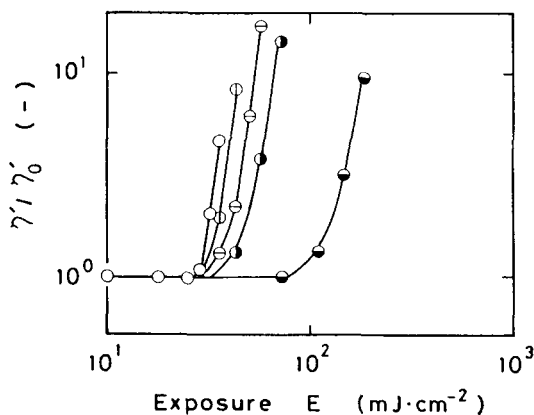


Fig. 5. Dependence of relative viscosity on the exposure energy at different film thicknesses for 5 wt% ZnO ink during UV curing: (○) 6.3 ; (◻) 15.7 ; (◻) 17.4 ; (●) 20.7 ; (◐) 38.4 μm .

and Kuhhirt⁷ have studied the curability of white-pigmented coatings with approximately equal hiding. According to their data, the cure rate of ZnO coatings is very slow compared with TiO_2 coatings when the pigment volume concentration is raised to 20%. The adverse effect of ZnO is very strong. In the present study, relatively high cure rates are obtained for ZnO inks. This may occur because the pigment volume concentration is lower than 6% and the curing is induced by a monochromatic light of 365 nm.

DISCUSSION

In earlier articles,^{2,4} we have discussed the curability of colored inks under 365 nm light in relation to the absorption of UV energy by the pigments. The increase of logarithmic plots of the minimum exposure energy with thickness is linear because the light intensity, that is, the UV energy absorbed by the photoinitiator exponentially decreases with depth in the film. In the inks containing highly absorbing pigments, the absorption by the pigments is an

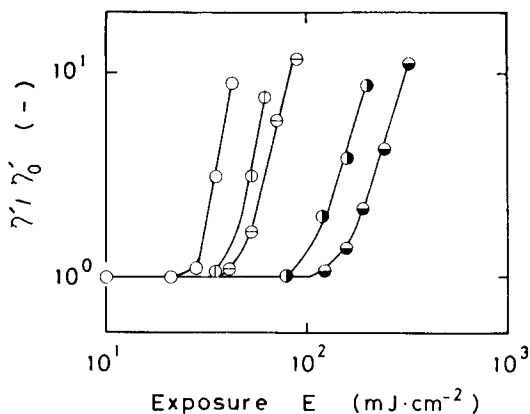


Fig. 6. Dependence of relative viscosity on the exposure energy at different film thicknesses for 10 wt% ZnO ink during UV curing: (○) 5.0 ; (◇) 9.2 ; (△) 14.3 ; (●) 22.2 ; (◐) 30.8 μm .

essential factor which determines the curability. The experimental results and theoretical prediction give the following equation:

$$E_m = E_0 \exp\{0.72(\alpha_i + \alpha_p)h\} \quad (1)$$

where h is the film thickness, E_0 is the minimum exposure energy for the vehicle at $h = 0$, giving the value for a thin film in which the degree of curing is considered to be homogeneous in the direction perpendicular to the shearing surface, and, α_i and α_p are, respectively, the absorption coefficient for the photoinitiator and for the pigment. The absorption coefficient for the photoinitiator is defined as $\alpha_i = 2.303\epsilon[I_n]$, where $[I_n]$ the concentration of photoinitiator with molar extinction coefficient ϵ . The absorption coefficient for the pigment is also proportional to the concentration of pigment. Equation (1) indicates that under conditions where the scattering of UV light by the pigments is negligibly small, the addition of absorbing pigment necessarily causes the reduction of cure rate.

To obtain further insight into the relation between the curability and the absorption of UV energy by the photoinitiator, the thickness dependence of the minimum exposure energy is examined as a first step. Figure 7 shows the results for TiO_2 inks and Figure 8 for ZnO inks. Since the plots for each ink lie on a straight line, it is inferred that the UV energy absorbed by the photoinitiator exponentially decreases with depth in the ink film. However, the most significant difference from the theoretical prediction is that the line for 5 wt% TiO_2 ink intersects the line for the vehicle at a thickness of 6 μm . Presumably, at thicknesses below this the ink gives higher cure rates than the vehicle. Considering that the potential of TiO_2 for hiding is great because of high refractive index, the strong dependence of the minimum exposure energy on the film thickness with relatively high cure rates may be coupled with its high scattering coefficient. The high scattering causes the increase in optical length of radiation in thin films, but at the same time causes the rapid attenuation of UV radiation in thick films. Figure 9 schematically shows the penetration of UV radiation in a TiO_2 ink. For thin films the cure rate is increased due to the

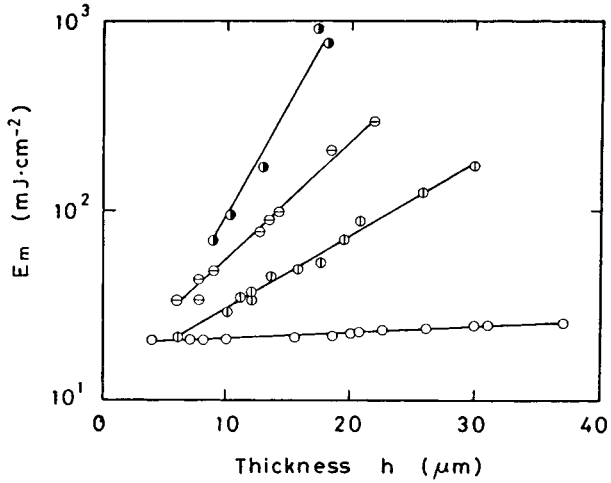


Fig. 7. Thickness dependence of the minimum exposure energy for inks containing TiO_2 at different concentrations: (○) 0; (◻) 5; (◻) 10; (●) 20 wt%.

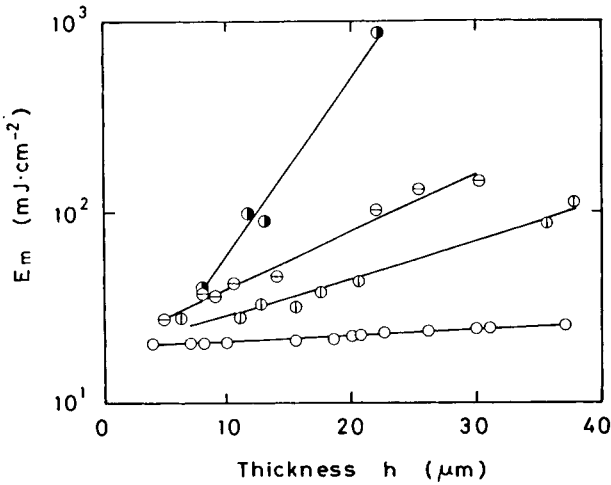


Fig. 8. Thickness dependence of the minimum exposure energy for inks containing ZnO at different concentrations: (○) 0; (◻) 5; (◻) 10; (●) 20 wt%.

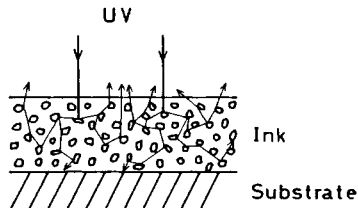


Fig. 9. Schematic illustration of penetration of UV radiation in a TiO_2 ink.

enhancement of UV absorption by the photoinitiator. However, for thick films it is greatly reduced due to the decrease in penetration depth of UV radiation.

Basic studies of the effect of pigments on the UV curing have been inhibited by the difficulty of calculating absorption of UV radiation by the photoinitiator in a film which scatters and absorbs radiation. Wicks and co-workers^{1,8} have theoretically investigated the absorption of UV radiation by the photoinitiators at the bottom of films on the basis of Kottler equation.⁹ Their model calculations indicate that in thin films the absorption by the photoinitiator is actually increased by the addition of the pigment.

We have already shown that the minimum exposure energy of colored ink film can be calculated from the UV absorption at the bottom of the film. In this study, the minimum exposure energy for TiO₂ ink films is predicted through the procedure proposed by Wicks and Kuhhirt.

Since the total radiation must be equal to the sum of reflected (R), transmitted (T), and absorbed (I) radiation, one can calculate the fraction of radiation absorbed by

$$I = 1 - (R + T) \quad (2)$$

Assuming that the fraction of radiation reflected by the surface of film can be ignored and transmitted radiation is absorbed by the substrate, the equations derived by Kottler are given as follows:

$$R = a - (T^2 + b^2)^{1/2} \quad (3)$$

$$T = b / \{a \sinh bSh + b \cosh bSh\} \quad (4)$$

$$a = \{(\alpha_i + \alpha_p) + S\} / S \quad (5)$$

$$b = (a^2 - 1)^{1/2} \quad (6)$$

where S is the internal scattering coefficient of ink film. Because the fraction of incident radiation absorbed by the pigment and the photoinitiator together can be calculated, the fraction absorbed by the photoinitiator alone, I_i , is given by

$$I_i = \{\alpha_i / (\alpha_i + \alpha_p)\} I \quad (7)$$

The absorption coefficient for the photoinitiator in the vehicle is estimated to be about 85 cm^{-1} from the molar extinction coefficient. However, this value should be modified because of increase in optical path length of radiation passing through the film due to the scattering by the pigment. The factor used for this purpose is found to be about 2.¹⁰ Since the pigment volume concentration of inks used in the present study is relatively low, the value of the factor changes in the range of 1.18 ~ 1.53, depending on the pigment concentration. The minimum exposure energy for the vehicle at $h = 0$ is determined to be $20 \text{ mJ} \cdot \text{cm}^{-2}$ from Figure 7. Therefore, once the absorption energy by the photoinitiator in the bottom layer of film is calculated, the minimum exposure energy of film with a given thickness is predicted by the procedure described previously.

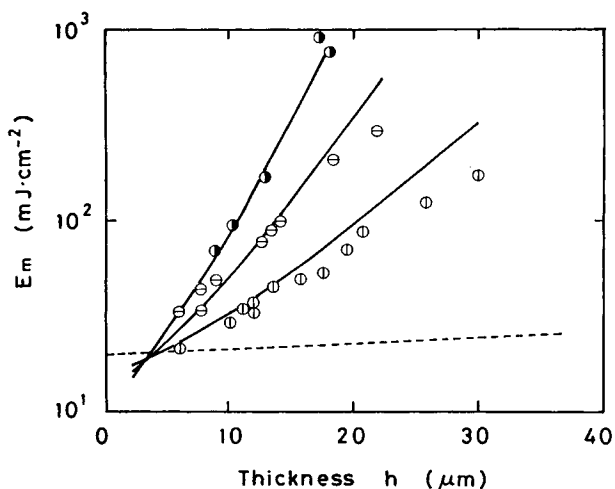


Fig. 10. Comparison of the theoretically predicted values of the minimum exposure energy (solid lines) with the experimental results (circles) for TiO_2 inks at different concentrations: (----) vehicle; (\circ) 5; (\ominus) 10; (\bullet) 20 wt%.

TABLE II
Values of α_i , α_p , and S for Theoretical Prediction

	5 wt% ink	10 wt% ink	20 wt% ink
α_i (cm^{-1})	100	115	130
α_p (cm^{-1})	300	450	600
S (cm^{-1})	2000	3500	5000

Figure 10 shows the calculated (solid lines) and experimental (circles) results for TiO_2 inks. The values of α_i , α_p , and S are shown in Table II. Although slight discrepancy can be seen at thickness larger than 20 μm , the theory shows a good agreement with experimental results. The UV energy absorbed by the photoinitiator in 10 μm films is estimated to be 7.5% for 5 wt% ink and 6.7% for 20 wt% ink. However, the absorption by the photoinitiator in the bottom 0.1 μm layer is 0.05% for 5 wt% ink and 0.02% for 20 wt% ink. The rapid increase in the minimum exposure energy with film thickness is caused by the precipitous decrease in absorption by the photoinitiator in the bottom layer of film.

CONCLUSIONS

The cure rate of UV inks containing white pigments was measured using an oscillating plate rheometer. Some of significant conclusions are as follows:

Since BaSO_4 has a refractive index very close to that of the vehicle and absorbs little light, BaSO_4 inks are rapidly cured as well as the vehicle.

Although ZnO inks show relatively high cure rates at thickness less than 10 μm , the hiding power is poor in the visible region.

For thin films of TiO_2 , the cure rate is very high because of the increase in optical path length by scattering. For thick films, the decrease in penetration

depth of UV radiation greatly reduces the cure rate. The minimum exposure energy can be theoretically estimated from the absorption by the photoinitiator at the bottom of film.

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