

## Application note 13

### Use of the Wetting Envelope

#### Task

The wetting properties of a solid with certain fluids, like inks, glues or varnishes, are very important in practice. In the present case, inks with different colour pigments (red, yellow and blue) are to wet film material so that they do not run, i.e. spread only very little, yet do not form too great a contact angle so that the coating is as thin as possible.

In a few cases the wetting of these fluids can be measured directly with the solid. But in many other cases, however, it is not possible to test various batches for their wetting properties during production.

With the application of the wetting envelope analysis, it is now possible to predict the contact angles of certain fluids on a defined surface without measuring them directly.

In the example shown, the surface free energy of the film is to be 40 mN/m, the polar contribution is 10 mN/m. The inks have the following surface tensions (determined from measurements of the interfacial tension):

Red ink = 39.0 mN/m; polar 9.0 mN/m

Yellow ink = 44.0 mN/m; polar 9.0 mN/m

Blue ink = 40.5 mN/m; polar 9.5 mN/m

#### Method

For a better understanding, it is first of all necessary to describe the mathematical background of the 'wetting envelope'. The method follows the calculation of interfacial interaction according to Owens-Wendt-Rabel-Kälble (OWRK).

The starting conditions for the consideration of a 'wetting envelope' first of all refer to the fact of the adhesion work according to Young, which is described as follows (symbols explained at end of text):

$$W_A = \sigma_i (1 + \cos \Theta) \quad (1)$$

For the adhesion work according to OWRK there applies:

$$W_A = 2 \left( \sqrt{\sigma_i^d \cdot \sigma_s^d} + \sqrt{\sigma_i^p \cdot \sigma_s^p} \right) \quad (2)$$

The surface tensions are divided into:

$$\sigma_i = \sigma_i^d + \sigma_i^p \quad (3)$$

For the complete wetting of the fluid, there applies:

$$\cos \Theta = 1 \quad (4)$$

From the equations (1) to (4), the following results:

$$\sigma_i^d + \sigma_i^p = \sqrt{\sigma_i^d \cdot \sigma_s^d} + \sqrt{\sigma_i^p \cdot \sigma_s^p} \quad (5)$$

The polar and dispersive contributions of a surface free energy can be entered into a coordinate system as a function. Hence, the wetting parameter R is obtained from a simple geometric consideration:

$$R = \sqrt{(\sigma_i^d)^2 + (\sigma_i^p)^2} \quad (6)$$

$$R \cdot \cos \varphi = \sigma_i^d \quad (7)$$

$$R \cdot \sin \varphi = \sigma_i^p \quad (8)$$

If (7) and (8) are included into (5), the result is (9)

$$R \cdot \cos \varphi + R \cdot \sin \varphi = \sqrt{R \cdot \cos \varphi \cdot \sigma_s^d} + \sqrt{R \cdot \sin \varphi \cdot \sigma_s^p}$$

Resolved to  $R$ , as a function of  $\varphi$ , the equation shows the value in the coordinate system for the complete wetting. As any polar or dispersive contribution cannot become negative, it is sufficient to consider this function for  $\varphi$  in the range of  $0-90^\circ$ . The equation for this function is:

$$R(\varphi) = \left( \frac{\sqrt{\cos \varphi \cdot \sigma_s^d} + \sqrt{\sin \varphi \cdot \sigma_s^p}}{\cos \varphi + \sin \varphi} \right)^2 \quad (10)$$

Evaluated for  $\varphi$  from  $0-90^\circ$ , this equation provides the 'wetting envelope' for a certain surface free energy. Outlined are the polar and dispersive contributions of the surface free energy. Fig. 1 shows such a relation for the values for the film.  $\sigma_s = 40$  mN/m; dispersive contribution  $\sigma_s^d = 30$  mN/m.

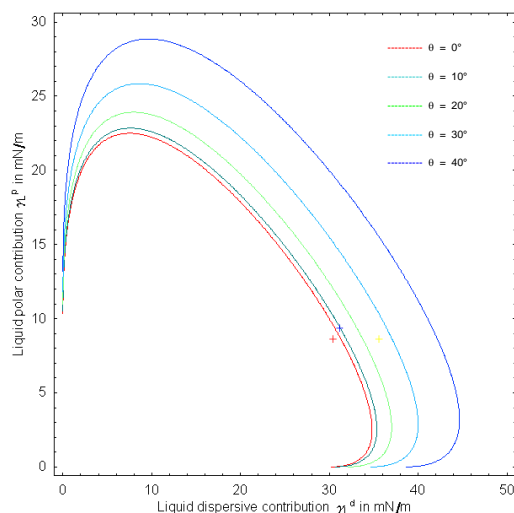


Fig. 1: Wetting envelope of film for  $0-40^\circ$ , with the values for the different ink colours

The relation  $R(\varphi)$  applies only for a complete wetting, i.e.  $\cos(\theta) = 1$ . If it is assumed now that a contact angle forms (e.g.  $10^\circ$ ), the parameter  $R$  must be multiplied by the factor  $2/(1+\cos(\theta))$ . This parameter  $R'$  now describes a wetting envelope for all angles  $\varphi$  with  $\theta=10^\circ$ . Such an extension is also shown in Fig. 1. Here, the wetting envelopes for  $\theta = 10^\circ, 20^\circ, 30^\circ$  and  $40^\circ$  were entered. This offers to the investigator the possibility to be better able to assess the wettability of the fluids to be examined.

Notation:

WA = Work of Adhesion in mN/m

$\sigma_s$  = Surface free energy of the solid in mN/m

$\sigma_{sd}$  = Surface free energy; dispersive contribution

$\sigma_{sp}$  = Surface free energy; polar contribution

$\sigma_l$  = Surface tension fluid in mN/m

$\sigma_{ld}$  = Surface tension; dispersive contribution

$\sigma_{lp}$  = Surface tension; polar contribution

$\theta$  = Contact angle in degree

$R, \varphi$  = Auxiliary polar coordinates to calculate the wetting envelope

## Results

The results are shown in Fig. 1. The value for the red ink is within the wetting envelope of  $\theta=0^\circ$ . This ink will fully spread on the film. The yellow ink is between the  $20^\circ$  and the  $30^\circ$  lines. The exactly calculated contact angle is  $25.3^\circ$ . The ink does not spread anymore, but forms quite a clear contact angle. This leads to a higher consumption of the ink. The blue ink is almost exactly on the  $10^\circ$  line ( $9.1^\circ$ ). This ink spreads only little and does not run. It forms a contact angle that keeps the drop volume very small and is therefore ideal for this film material.

## Summary

By means of the wetting envelope, the three inks could be characterised in their wetting properties without actually measuring them on the film surface. The method therefore offers to the user the opportunity to make such examinations with surface and/or fluids already characterised in a quick and also cost-effective way.