

# Low volatile organic compounds coatings: surface energy considerations

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**ABSTRACT:** *With increasingly stringent EPA guidelines for controlling emission of volatile organic compounds (VOC), the need for lower VOCs in inks and coatings is evident. When overprinting of inks is required, the wettability of ink by the coating is important. This paper presents the role of surface energy in achieving good printability in overprinted systems. Surface energies, determined from measured contact angles of water and methylene iodide on dry ink film or dry coating, are correlated with printability and product properties.*

**KEYWORDS:** *Coating, printability, surface energy, volatiles content.*

In one paper, Bassemir and Krishnan (1) compared the dynamic surface tension of a solvent-based ink with two water-based inks. Their conclusion was that most solvent-based inks tend to have fairly low dynamic surface tensions. Water-based inks are more likely to exhibit problems due to the inherent high surface tension of water and the use of inappropriate surfactants or vehicle chemistry. Therefore, low dynamic surface tension is an important factor in achieving superior film formation, good wetting, and printability in waterborne coatings and inks.

To obtain dynamic surface tension readings of waterborne systems similar to solvent-based systems, the amount of alcohol included in the

formulation is approximately 20–25% (2, 3). Tighter EPA regulations aimed at reducing VOCs have led the search for more efficient surface tension reducers—surfactants. The challenge for surfactants to replace alcohols lies in developing products that achieve a delicate balance between compliance and performance. It is more difficult to accomplish this for low VOC waterborne coatings or inks (systems). (Low VOC here is defined as organic volatile compounds, as defined by EPA Method 24, from 5% to 10% by weight of a total ink or coating.)

Because of these restrictions, the use of waterborne latex-based systems is expanding into other areas traditionally reserved for organic

solvent-based systems. In Winnik and Wang's (4) article, the authors discuss the role of surfactants (coalescing aids) in film formation and the importance of film formation of coating in protecting the underlying materials.

It was the writer's intent to understand the cause or causes of poor lay or "orange peel" typically observed in water-based coatings. When the orange peel effect is observed in water systems, the solution to this problem would be to lower the dynamic surface tension of the coating by using alcohols or surfactants or both within compliance. However, the addition of alcohol or the addition of surfactants or both did not help to resolve the problem completely this time. This partial solution motivated the writer to investigate the problem and to uncover the hidden clues to solve the mystery.

### The Young equation

The theory used in this paper is based on the surface energy of a solid defined in Janczuk's work (5). It is defined as:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

To express the interfacial free energy of solid-liquid or liquid-liquid as a function of the geometric mean of dispersion and nondispersion intermolecular interaction we can write:

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$$\gamma_L \cos \theta_1 = -\gamma_L + (\gamma_L^d \gamma_s^d)^{1/2} + 2(\gamma_L^p \gamma_s^p)^{1/2} \quad (2)$$

Where L and S refer to liquid and solid, d and n refer to dispersion and nondispersion, respectively. Theta is the contact angle measured. Measuring the contact angle for a given liquid on the surface of two different solids for which the values of  $\gamma_s^d$  and  $\gamma_s^n$  are known, the  $\gamma_L^d$  and  $\gamma_L^n$  values can be calculated easily from Eq. 2, which can be rewritten as:

$$\gamma_L (\cos \theta_L + 1)/2 = (\gamma_L^d \gamma_s^d)^{1/2} + (\gamma_L^n \gamma_s^n)^{1/2} \quad (3)$$

When surface energy of a solid results only from dispersion intermolecular interactions,  $\gamma_s^n$  can be assumed approximately equal to zero. This term  $(\gamma_L^n \gamma_s^n)^{1/2}$  can be ignored. Equation 3 becomes:

$$\gamma_L (\cos \theta_L + 1)/2 = (\gamma_L^d \gamma_s^d)^{1/2} \quad (4)$$

With  $\gamma_s = \gamma_s^d$ , Eq. 4 can be expressed as follows after being squared:

$$\gamma_L^2 (\cos \theta_L + 1)^2/4 = \gamma_L^d \gamma_s^d \quad (5)$$

Rearranging Eq. 5:

$$\gamma_L^2 (\cos \theta_L + 1)^2/4 \gamma_s^d = \gamma_L^d \quad (6)$$

Equation 6 is the Young equation for low surface energy of a solid surface.

The surface energy calculations in this study were based on Eqs. 3 and 6. After measuring the contact angles of water and methylene iodide, of which  $\gamma_L^d$  and  $\gamma_L^n$  are known, the values of  $\gamma_s^d$  and  $\gamma_s^n$  can be resolved easily. The total surface energy of the surface of an unknown solid can be calculated by Eq. 1, after the values of  $\gamma_s^d$  and  $\gamma_s^n$  are obtained.

## Experimental

A surface coating was used to evaluate the effect of the surface energies of 15 experimental inks on the performance of the coating.

As mentioned previously, low dynamic surface tension in inks is important for printing on the substrate. The dynamic surface tension of 15

### I. Test inks

| Component         | Control | Group I |        |        |        |  |
|-------------------|---------|---------|--------|--------|--------|--|
|                   |         | Exp. A  | Exp. B | Exp. C | Exp. D |  |
| Resin             | 69      | 69      | 69     | 69     | 69     |  |
| Base              | 20      | 20      | 20     | 20     | 20     |  |
| Defoamer          | 0.5     | 0.5     | 0.5    | 0.5    | 0.5    |  |
| Wax emulsion      | 2.0     | 2.0     | --     | --     | --     |  |
| Resolubility aids | 3.0     | --      | 3.0    | --     | --     |  |
| Surfactant        | 3.0     | --      | --     | 3.0    | --     |  |
| Hydrotrope        | 2.5     | --      | --     | --     | 2.5    |  |
| Water             | 0.0     | 8.5     | 7.5    | 7.5    | 8.0    |  |

| Component         | Control | Group II |        |        |        |        |        |
|-------------------|---------|----------|--------|--------|--------|--------|--------|
|                   |         | Exp. E   | Exp. F | Exp. G | Exp. H | Exp. I | Exp. J |
| Resin             | 69      | 69       | 69     | 69     | 69     | 69     | 69     |
| Base              | 20      | 20       | 20     | 20     | 20     | 20     | 20     |
| Defoamer          | 0.5     | 0.5      | 0.5    | 0.5    | 0.5    | 0.5    | 0.5    |
| Wax emulsion      | 2.0     | 2.0      | 2.0    | 2.0    | --     | --     | --     |
| Resolubility aids | 3.0     | 3.0      | --     | --     | 3.0    | --     | 3.0    |
| Surfactant        | 3.0     | --       | 3.0    | --     | 3.0    | 3.0    | --     |
| Hydrotrope        | 2.5     | --       | --     | 2.5    | --     | 2.5    | 2.5    |
| Water             | 0.0     | 5.5      | 5.5    | 6.0    | 4.5    | 5.5    | 5.5    |

| Component         | Control | Group III |        |        |        |
|-------------------|---------|-----------|--------|--------|--------|
|                   |         | Exp. K    | Exp. L | Exp. M | Exp. N |
| Resin             | 69      | 69        | 69     | 69     | 69     |
| Base              | 20      | 20        | 20     | 20     | 20     |
| Defoamer          | 0.5     | 0.5       | 0.5    | 0.5    | 0.5    |
| Wax emulsion      | 2.0     | 2.0       | 2.0    | 2.0    | --     |
| Resolubility aids | 3.0     | 3.0       | --     | 3.0    | --     |
| Surfactant        | 3.0     | 3.0       | 3.0    | --     | --     |
| Hydrotrope        | 2.5     | --        | 2.5    | 2.5    | --     |
| Water             | 0.0     | 2.5       | 3.0    | 3.0    | 10.5   |

### II. Results for Group I inks

| Inks   | Surface energies, dynes/cm |            |       | Dynamic surface tension, dynes/cm | Ink index <sup>a</sup> | Coating index <sup>a</sup> | Gloss 60° |
|--------|----------------------------|------------|-------|-----------------------------------|------------------------|----------------------------|-----------|
|        | Total                      | Dispersion | Polar |                                   |                        |                            |           |
| Exp. A | 57                         | 40         | 17    | 52                                | 1                      | 3                          | 66.3      |
| Exp. B | 59                         | 38         | 21    | 55                                | 2                      | 2                          | 66.0      |
| Exp. C | 48                         | 39         | 9     | 38                                | 4                      | 1                          | 47.8      |
| Exp. D | 55                         | 29         | 26    | 45                                | 3                      | 4                          | 70.4      |

<sup>a</sup> 1 worst (orange peel); 4 best (smoothness)

### III. Results for Group II inks

| Inks   | Surface energies,<br>dynes/cm |            |       | Dynamic<br>surface tension,<br>dynes/cm | Ink<br>index <sup>a</sup> | Coating<br>index <sup>a</sup> | Gloss<br>60° |
|--------|-------------------------------|------------|-------|-----------------------------------------|---------------------------|-------------------------------|--------------|
|        | Total                         | Dispersion | Polar |                                         |                           |                               |              |
| Exp. E | 56                            | 31         | 25    | 57                                      | 1                         | 5                             | 70.1         |
| Exp. F | 46                            | 36         | 9     | 40                                      | 4                         | 2                             | 52.4         |
| Exp. G | 58                            | 28         | 30    | 48                                      | 2                         | 6                             | 69.4         |
| Exp. H | 55                            | 31         | 24    | 38                                      | 5                         | 3                             | 49.9         |
| Exp. I | 45                            | 39         | 6     | 44                                      | 6                         | 1                             | 46.8         |
| Exp. J | 53                            | 31         | 23    | 47                                      | 3                         | 4                             | 69.4         |

<sup>a</sup> 1 worst (orange peel); 6 best (smoothness)

### IV. Results for Group III inks

| Inks   | Surface energies,<br>dynes/cm |            |       | Dynamic<br>surface tension,<br>dynes/cm | Ink<br>index <sup>a</sup> | Coating<br>index <sup>a</sup> | Gloss<br>60° |
|--------|-------------------------------|------------|-------|-----------------------------------------|---------------------------|-------------------------------|--------------|
|        | Total                         | Dispersion | Polar |                                         |                           |                               |              |
| Exp. K | 51                            | 33         | 18    | 46                                      | 3                         | 2                             | 48.7         |
| Exp. L | 49                            | 38         | 11    | 39                                      | 4                         | 1                             | 46.7         |
| Exp. M | 55                            | 31         | 24    | 46                                      | 2                         | 3                             | 64.3         |
| Exp. N | 55                            | 30         | 25    | 51                                      | 1                         | 4                             | 69.0         |

<sup>a</sup> 1 worst (orange peel); 4 best (smoothness)

### V. Summary

| Inks    | Surface energies,<br>dynes/cm |            |       | Dynamic<br>surface tension<br>dynes/cm | Ink<br>index <sup>a</sup> | Coating<br>index <sup>a</sup> | Gloss<br>60° |
|---------|-------------------------------|------------|-------|----------------------------------------|---------------------------|-------------------------------|--------------|
|         | Total                         | Dispersion | Polar |                                        |                           |                               |              |
| Exp. C  | 48                            | 29         | 19    | 39.6                                   | 4                         | 1                             | 47.8         |
| Exp. I  | 45                            | 39         | 6     | 13.3                                   | 6                         | 1                             | 46.8         |
| Exp. L  | 49                            | 29         | 20    | 40.8                                   | 4                         | 1                             | 46.7         |
| Exp. D  | 55                            | 29         | 26    | 43.6                                   | 3                         | 4                             | 70.4         |
| Exp. G  | 58                            | 28         | 30    | 51.7                                   | 2                         | 6                             | 69.4         |
| Exp. N  | 55                            | 30         | 25    | 45.5                                   | 1                         | 4                             | 69.0         |
| Control | 55                            | 35         | 20    | 36.4                                   | 6                         | 1                             | 47.6         |
| Coat A  | 59                            | 28         | 31    | 52.5                                   | --                        | 6                             |              |

<sup>a</sup> 1 worst (orange peel); 6 best (smoothness)

### VI. Surface energy components for water and methylene iodide

| Fluid            | Total<br>surface energy,<br>dynes/cm | Dispersion<br>component | Polar<br>component |
|------------------|--------------------------------------|-------------------------|--------------------|
| Water            | 72.8                                 | 50.8                    | 22                 |
| Methylene iodide | 50.8                                 | 50.8                    |                    |

experimental inks was measured. Then, total surface energies, polar components, and dispersion components of 15 dry ink films were calculated using the Young equation.

In this study, surface tension is defined as the intermolecular forces of attraction between neighboring molecules in liquids. Surface energy is defined as the intermolecular forces of attraction between neighboring molecules in solids.

### Sample preparation

The experimental ink was used to prepare 15 different formulas (Table II). The basic ingredients in the experimental ink formula are resin, base, defoamer, wax emulsion, resolubility aids, surfactants, a hydrotrope, and water. Wax emulsions, resolubility aids, surfactants, and hydrotropes were chosen as test parameters because they would most likely change the characteristics of a surface.

Conventionally, wax emulsions, which contain emulsifiers, would normally migrate to the surface. The orientation of wax molecules results in surface changes.

Resolubility aids are used in formulation to maintain rewettability when a printing cylinder on the press is restarted. To achieve rewettability, resolubility aids always contain a water-loving group in their chemical structure. Surface changes could possibly happen because of the rearrangement on the surface caused by these water-loving groups.

Surfactants are classified as substances which contain a hydrophilic head and hydrophobic tail. A surfactant normally diffuses rapidly in liquid media. When it diffuses to the air/water interface the surface chemistry is changed as the hydrophilic head faces water molecules and the hydrophobic tail faces air (7).

Hydrotropes are organic molecules that will move in response to water, resulting in movement to the surface and changing the surface alignment.

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Table II lists all the inks used and categorizes the inks into Group I, II, III, and control. For example, Exp. A in Group I contains resin, base, defoamer, resolubility aid, and water. The ratio of resin to base was kept constant. The amount of defoamer was fixed. Water was used to bring formula to 100%. Inks in Group II differ in their combination of test parameters. For instance, Exp. E differs in the combination of resolubility aid and wax emulsion from the combination of wax emulsion and surfactant in Exp. F. In Group III, inks contain three test parameters in each formula. All the changes in test parameters were designed to investigate the effects of these changes on the smoothness of the coating. All the inks were printed on board (substrate) for contact angle measurements.

### Surface energy measurement

A goniometer was used to measure the surface energy of the dry ink films by measuring contact angles of water and methylene iodide. The polar and the dispersion forces were calculated using the Young equation

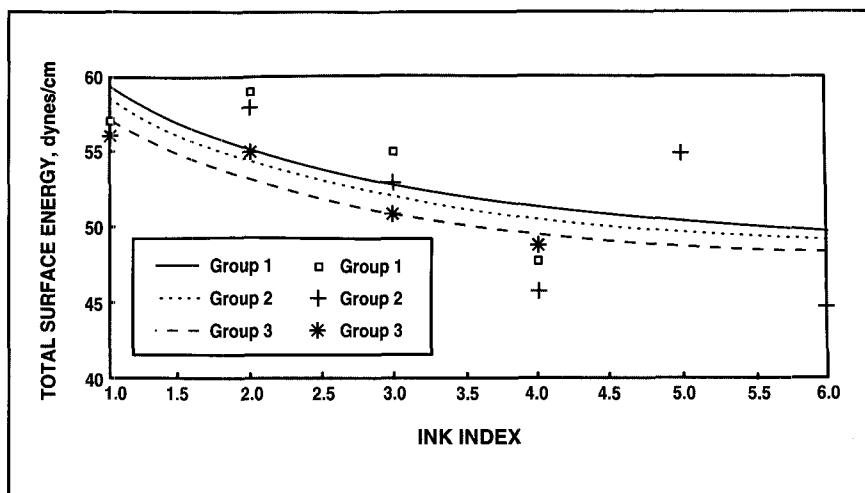
### Dynamic surface tension measurements

A surface tensiometer 6000, from Chem-Dyne Research Corp., was used to acquire dynamic surface tension readings. This apparatus, comprised of a pair of tubes having orifices of different diameters positioned below the surface of the liquid, measures the differential pressure to generate a bubble in the tubes as a function of the surface tension of the liquid (8).

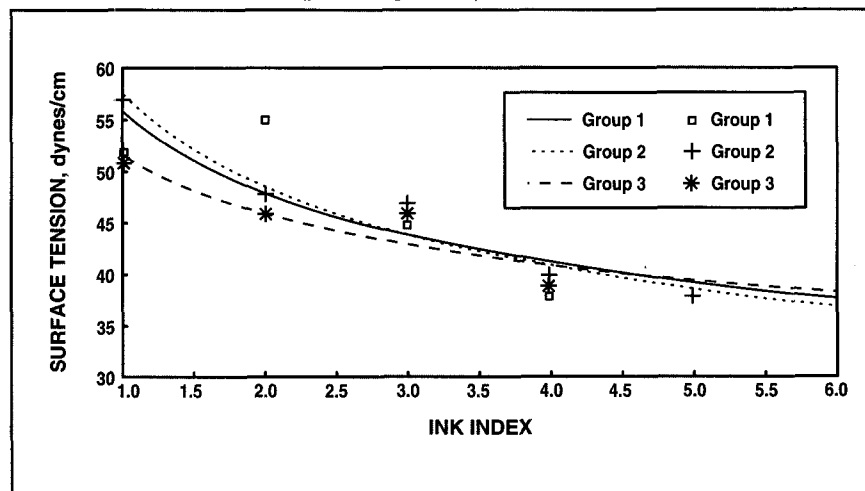
### Product properties

Printability ("orange peel" appearance), gloss, total surface energy, polar and dispersion components, and the percent of polarity were evaluated. The "orange peel" of inks and coatings were rated as Ink Index (the rating of ink printability)

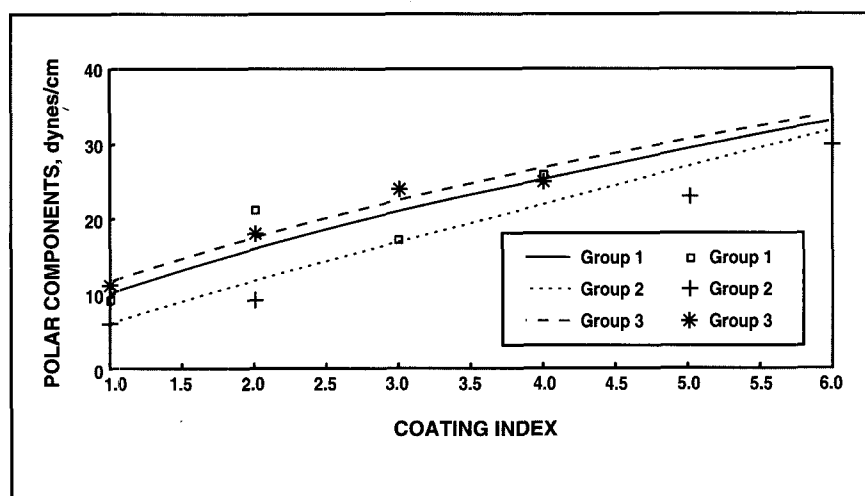
1. Surface energies of dry ink film (power regression)



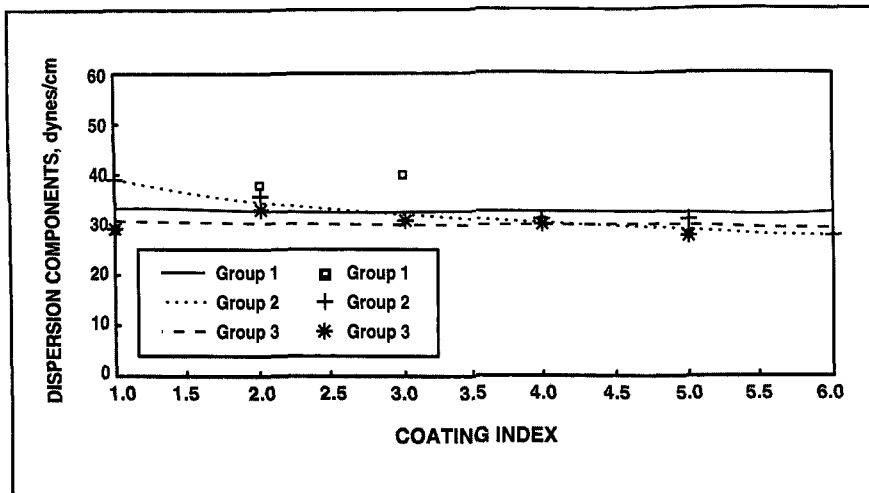
2. Surface tension of wet inks (power regression)



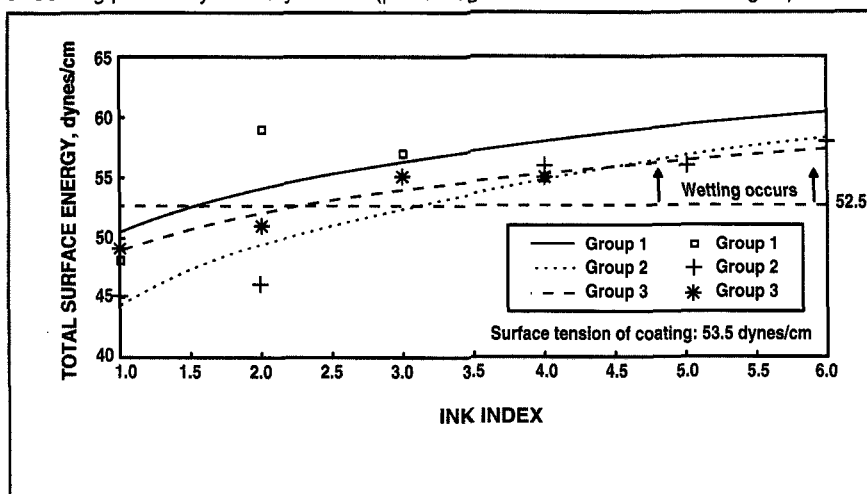
3. Coating printability over dry ink film (power regression of polar components)



#### 4. Coating printability over dry ink film (power regression of dispersion components)



#### 5. Coating printability over dry ink film (power regression of total surface energies)



and Coating Index (the rating of coating printability) in Tables I and III-VI.

### Results and discussion

Tables III, IV, and V display the data of surface characteristics of all the experimental inks. In each group, it was observed that high total surface energy inks provide a better environment for the overprint lacquer to lie smoothly on the surface of the ink. Gloss readings of the lacquer over high and low total surface energy inks indicate that higher surface energy inks were required for a lacquer to print smoothly.

#### Influence of total surface energy of dry ink on ink printability

Extensive studies have been conducted to correlate the printability of ink to dynamic surface tension, but little research has been done on total surface energy of ink film to ink printability. Figure 1 shows that the lower total surface energy of ink film the better the ink lay (see the total surface energy readings in ink F, I, K, and L).

It was also found that the formula which gives the best ink lay includes a surfactant. For example, Exp. C, Exp. I and Exp. L, rated as the best ink lay in each group, contains a surfactant in its formula. These inks

also have fairly low dynamic surface tension. However, they gave the worst coating lay because of the divergence in the polar component values.

#### Influence of dynamic surface tension of wet inks on ink smoothness (printability)

Lower dynamic surface tension of inks gives better ink lay (Fig. 2). Each group of inks demonstrates the same tendency. Inks rated as 1 and 2 (Fig. 2) displayed poor print quality, which can be interpreted as the effect of not using surfactants as dynamic surface tension reducers (Table II).

#### Relationship of polar and dispersion components of inks to coating printability

Good coating lay is observed in Fig. 3 as the inks' polar component matches the coating's polar component. The polar component values ranged from 25 to 31 dynes/cm (Fig. 3). This was needed to obtain good coating printability in this evaluation. Very little effects of dispersion components can be observed in Fig. 4.

Polarity of the solid surface is another important factor that helps to characterize properly the surfaces compared in this work. It can be expressed as:

$$\% \text{ Polarity} = 100\% \times \frac{\text{Polar components}}{\text{Total surface energy}} \quad (7)$$

Table VI lists the ratings of ink printability, of coating printability, and percent polarities. The trend suggests that the ink having a percent polarity closest to the coating's polarity yields the best coating appearance.

#### Relationship of coating printability to total surface energy of dry ink film

The dynamic surface tension of the coating was measured to be 52.5 dynes/cm. For wetting to occur, the

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surface energy of the underlying material (dry ink film) should be higher than 52.5 dynes/cm. Good coating printability is displayed in Fig. 5 when the total surface energies of the dry ink films ranged from 55 dynes/cm to 58 dynes/cm.

### Conclusions

In the absence of surfactants, inks have high total surface energy and high dynamic surface tension. Excellent coating lay was obtained by laying the coating over these inks. Poor quality of ink lay was also observed. These observations indicate that the presence of surfactant in the evaluation is critical.

In addition, the choice of a minimum level of total surface energy for good coating printability is based on the choice of dynamic surface tension of the wet coating. In this study,

the choices were limited because the surface coating was required for the specific product properties. Changing the underlying ink system solved the "orange peel" problem.

It is evident that a lower coating dynamic surface tension will be helpful in solving the "orange peel" problem of the surface coating. With the very rigid VOC regulation, the addition of alcohols is not a valid solution for today's technology. Solution of the problem should be geared to the choice of latex or resin systems in the surface coating because the formation of waterborne latex systems will help the formulator select an adequate printing dynamic surface tension for surface coatings. **□**

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