Mechanisms leading to a defect in some solvent-coated films

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Under certain circumstances, small circular voids appear in gravure-coated films. These voids may be arranged so that there is one void corresponding to each cell of the gravure cylinder, or develop into chains of larger voids, or have a two-dimensional pattern, the most stable of these having the voids located at the vertices of a hexagonal pattern, as shown in lower images of Fig. 1. In this specific case, the defect is formed by a combination of mechanisms that hinge on the following, fairly common, conditions:

- The coating material consists of a mixture of two miscible solvents with significantly different equilibrium vapor pressures, with the lower one (e.g., toluene) having a higher surface tension than the solvent with the higher vapor pressure (e.g., methanol).

- Trace amounts of a third liquid (e.g., water) with the highest surface tension but lowest equilibrium vapor pressure, and soluble in the solvent with the higher vapor pressure but insoluble in the other solvent.

To understand the process, it is convenient to first examine the pumping effects of a single drop and then to pay attention to the interaction between drops. To simplify the description, the different liquids will be referred to as toluene, methanol, and water, but it should be clear that the process applies more generally and depends on the relative characteristics described in the bullets above.

A single drop of water lies in a film composed of the two solvents, as shown if Fig. 2. The surface tension above the drop, which is an aqueous solution, is higher than the surrounding film, so a surface tension gradient is formed. Liquid at the free surface is dragged towards the drop. Solvent evaporates, especially the high vapor pressure component, methanol. Furthermore, methanol dissolves in water, reducing its concentration in the film. The toluene-enriched liquid that is rejected by the drop must flow away, driven by pressure gradients caused by the varying curvature of the film's free surface. Because the surface tension of methanol is lower than that of toluene (24 vs. 28 dyne/cm), the film is not destabilized.

As should be clear from this description, the drop becomes an efficient scrubber of the toluene, removing all materials soluble in water and rejecting the remainder. Among these there may be traces of water that are

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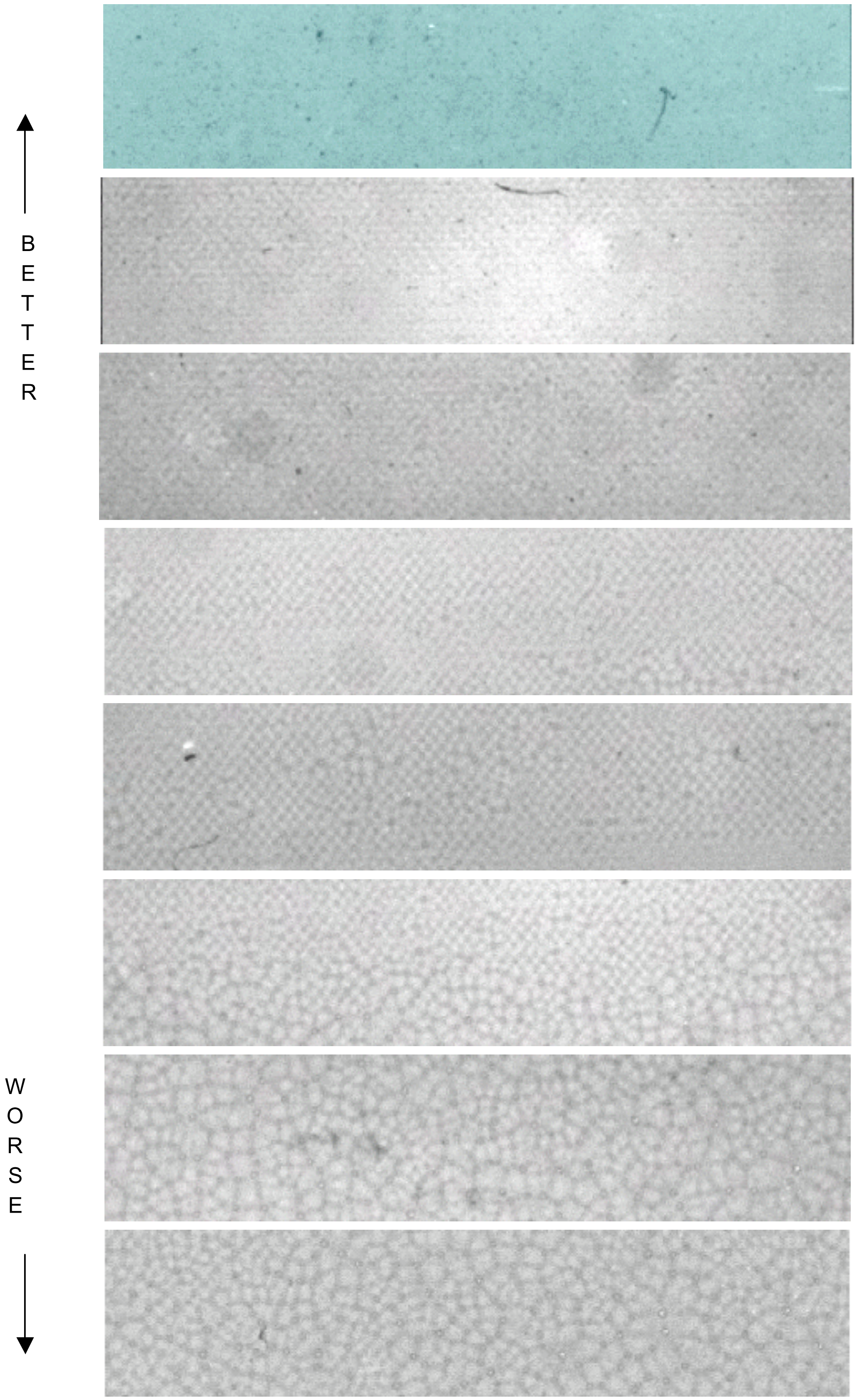

Figure 1. Different severity levels of the defect. Each image represents a strip of dimensions 0.12×0.51 in.^{2} (3×13 mm^2).

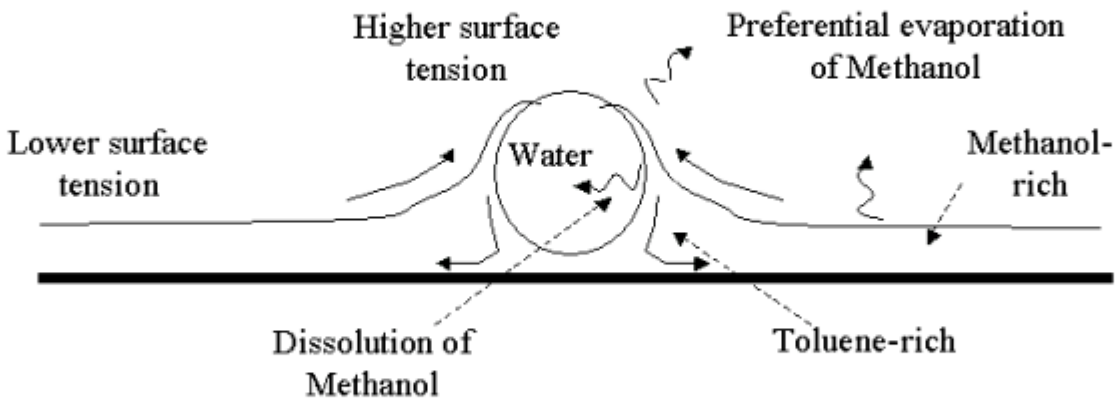

Figure 2. Pumping effect of water drops in a film of toluene and methanol..

also in the continuous phase which, because of their lower equilibrium vapor pressure, tend to be collected in the drop and cause it to grow. The traces of water may have been in solution from the beginning or may have resulted from condensation. This is the simplistic description of the water drop acting like a pump and scrubber.

Figure 1 shows that drops tend to grow in size and reduce their population per unit area. Another mechanism of growth, therefore, must be coalescence. As the drops scrub the solution of methanol and traces of water, the region between drops that are nearest neighbors will have been scrubbed more effectively. The surface tension in these areas ought to be closer to that of its main component, toluene, which is higher than for methanol and, therefore, for the regions less well scrubbed. The regions of higher surface tension will tend to contract, bringing the drops closer to each other and, eventually, to coalesce. Further evidence of the contraction of the free surface in these regions is the line of higher density connecting neighboring drops, shown in the lower images of Fig. 1, indicating that more dye has been deposited in these regions.

This tendency of neighboring drops to attract each other can be used to explain why droplets tend to align themselves. A drop near a chain where the that drop is roughly equidistant from two other drops will be attracted to the chain by the resultant force; if it is closer to one drop, the region between the two will be more depleted of methanol, and thus have a higher surface tension, tending to contract that free surface and the two drops coalescing. It appears that the most stable arrangement occurs when each drop has three nearest neighbors, each equidistant to it and also equidistant between the three, as shown in Fig. 3. This is the basic building block for the hexagonal-shaped cells seen when the defect is most developed..

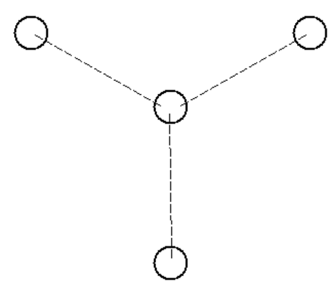

Figure 3. Basic building block of hexagonal cell pattern.

Several bench-top experiments have been performed that support the described mechanisms. First, the solubility isotherms of water were measured for different ratios of the solvent mix. This information can be used, in combination with a model of the drying process of a coated film, to predict whether water, which condenses onto the coating in the drying process, could reach sufficiently high concentrations to come out of solution. In the example shown during this presentation, this is indeed the case.

A second bench-top experiment consists of observing the behavior of a water droplet in a thick (500 μm) film of the organic solvents at different temperatures in the absence and presence of some surfactant. If possible, short movies will be shown demonstrating typical behaviors. For example, Fig. 4 shows two still images 45 seconds after the water droplet has been inserted. The film in the left image has no surfactant, while the one on the right contains traces (0.3% w/w) of Fluorad FC430. The dark coloring is produced by a nigrosine dye soluble in water but insoluble in toluene, which was mixed with the organic solvents. Note that a lot of the dye has been transferred to the drop on the left, but not to the drop on the right. Indeed, the solution shown on the left is much more susceptible to the scrubbing mechanism described earlier.

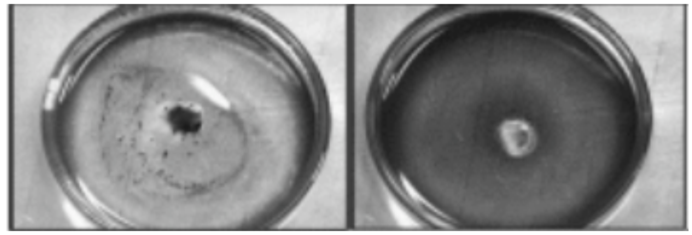

Figure 4. Still images taken of a film at 40 ºC, 45 s after a water droplet has been placed at its center. The solution on the right contains traces of the surfactant Fluorad FC430..

A last experiment shows water condensing on the surface of the film, the resulting formation of water droplets, coalescence, and motion. While the conditions do not replicate those of the coatings shown in Fig. 1, it is clear that the mechanisms described are inherent to these types of solvent mixtures when in the presence of trace amounts of water.

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