Photomicrographic Determination of Free Film Swelling

The significance of swelling as a major factor in coating film quality has been emphasized strongly in the recent literature.[1-4] The effects of moisture in particular on polymeric coatings are studied extensively by measuring the water-induced swelling of free films, both pigmented and unpigmented. Equilibrium water uptake data are generally obtained by measuring changes in film area[5] or weight[3] after prolonged immersion. To determine rates of change with these methods, many samples must be prepared and immersed and then individually withdrawn and measured. Both rate and equilibrium data are secured by these techniques at considerable cost in time and effort and even then are open to question, since it is not the actual swelling that is measured but rather some function of it that survives the subsequent manipulations. Brunt's microscope technique[6] improves upon the other methods by measuring swelling directly and by reducing both the number of samples and number of manipulations required in a given study, but even his method is very difficult to use in the early stages of swelling when the rate of change in film dimensions is greatest. Replacing the human eye in Brunt's technique with a camera retains the advantages of his method while providing for instantaneous measurements.

A Bausch and Lomb laboratory microscope fitted with a Romicron camera using Polaroid pack film was employed throughout. All photographs were taken through a 3.5 × objective and 5× hyperplane eyepiece. The total magnification was 8.75× because the camera itself contains a 0.5× lens. Square or triangular samples of 2–4 mm. edge length were cut from films that had been drawn down on Teflon sheet and dried and aged under controlled temperature and humidity. The samples were laid flat on standard 1 × 3 in. microscope slides, photographed, then covered with a drop of water and a coverslip and photographed periodically. The ratio of image area at time t after wetting to the image area of the unwetted sample is equal to the sample area ratio, since all photographs are taken at constant magnification.

To determine image area ratios, the images were cut from the uncoated Polaroid prints and weighed. Possible sources of error that were investigated and found not to contribute more than a few tenths of a per cent to the stanard deviation of a series of repeat measurements were: uniformity of the Polaroid print both in one pack and between different packs, possible lens effect of the water on the sample, small variations in developing time of the prints, and the cutting operation itself. The coating step recommended by the

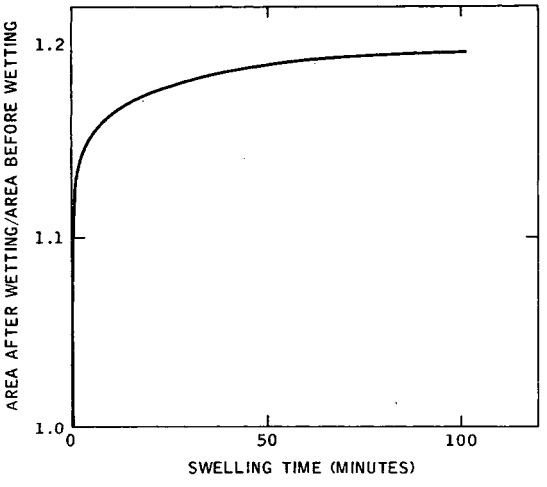

Fig. 1. Time–swelling curve for a commercial acrylic latex (Rohm and Haas Rhoplex AC-34) pigmented with TiO_2 and $CaCO_3$ to 35% pigment volume concentration.

manufacturer to "permanentize" the prints must be omitted because it provied impossible to manipulate uniformly the swab supplied with the film.

A typical curve is shown in Figure 1. To get an estimate of the "smoothness" of the data regression analyses were performed with an IBM 7094 computer to obtain analytic expressions for the observed dependence of area on time. While no theoretical significance was attached to the computed equations they did provide a basis for statistical analyses. In all instances the standard error was less than 2%, suggesting strongly that the data were not erratic.

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