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A Threshold Phenomenon in Coating Porous Surfaces with Aerosols. Applications to Antitranspirant Delivery.

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Transpiration from the leaves of plants results in enormous consumption of water supplies. The extent of irrigation needs in agriculture, and sometimes the feasibility of certain crop production in arid lands, is largely determined by this factor. Since 99% of the water which enters a plant is transpired (Gale and Hagan, 1966)—*i.e.*, only 1% is retained to sustain the life processes—there is abundant incentive to seek methods of reducing this loss. Unlike many other water "losses" in agriculture, transpiration of water to the air is irrecoverable in a given area and season. Therefore, in arid and semi-arid areas with limited water supplies, efficient and cheap methods of reducing transpiration (preferably with minimal impact on CO_2 and O_2 exchange) are important. This is particularly true when projected water demands can exceed current supplies in many regions of the world.

Extensive experimentation has been conducted with antitranspirants (*AT's*) to suppress passage of water vapor through stomata to conserve water (Waggoner and Turner, 1971; Davenport, *et al.*, 1976) and improve plant water potential (Davenport, *et al.*, 1974), although it is recognized that passage of other gases will also be affected by such methods. One of the common strategies is to occlude the stomata with a thin physical barrier to retard diffusion, and such an *AT* is usually delivered as a spray or an aerosol. Such strategies have had only limited success; the difficulty is apparently caused by incomplete coverage of the leaf surface. This is due in part to the practical problem of delivering the *AT* to leaf canopies from ground rigs or aircraft. A more fundamental problem is that spray droplets may occlude stomata directly at the impact point, but since spreading apparently does not occur many stomata remain exposed (Fisher and Lyon, 1972).

To facilitate rapid screening of *AT's* being designed for better spreading, a simple model system was constructed to simulate many features of the gas-exchange performance of real stomata (Erickson, 1978). The porous polycarbonate membranes made by Nuclepore Corp. (Pleasanton, CA) have uniform cyclindrical pores of suitable dimensions. Membranes selected for this study had nominal pore diameters $d = 0.8, 5, 10\ \mu m$, with lengths 10, 10, 8 μm and pore (void) fractions 0.151, 0.078, 0.078 respectively. Each membrane was mounted in a glass cell and tested for either water vapor transport in a stagnant environment (Figure 1a) or for CO_2 or O_2 transport in a flowing-gas environment (Figure 1b). The CO_2/O_2 study is a significant advance over most previous *AT* investigations, which have usually been limited to measurements of water transport only.

Membranes were tested both with and without coatings. Coatings of various liquids were applied by aerosol deposition in a large flow-through chamber fed continuously by a DeVilbiss nebulizer. Silicones—chosen because of promising results with actual plants (Angus and Bielorai, 1965)—and a pure vegetable oil (*VO*) consisting of soybean and cottonseed oils, were deposited by this technique. A commercial *AT*, Wilt Pruf from Nursery Specialty Products (Greenwich, CT) was also used but the nebulizer was less effective, and a hand-operated plant mister and multiple applications were required to obtain deposition of films comparable to the 20 cs-silicone and *VO* used in most of this work.

Aerosol particle sizes were quite uniform, the number-distribution having a sharp maximum at 1.1 μm as measured with a Climet optical analyzer. Except for Wilt Pruf coating, membranes remained in the settling chamber until the desired degree of deposition D (in kg/m^2 of membrane area) had occurred, as determined by weighing. Membranes of known D were then loaded into test cells and evaluated for H_2O, CO_2, and O_2 transmission. For the uncoated case ($D = 0$), a special set of

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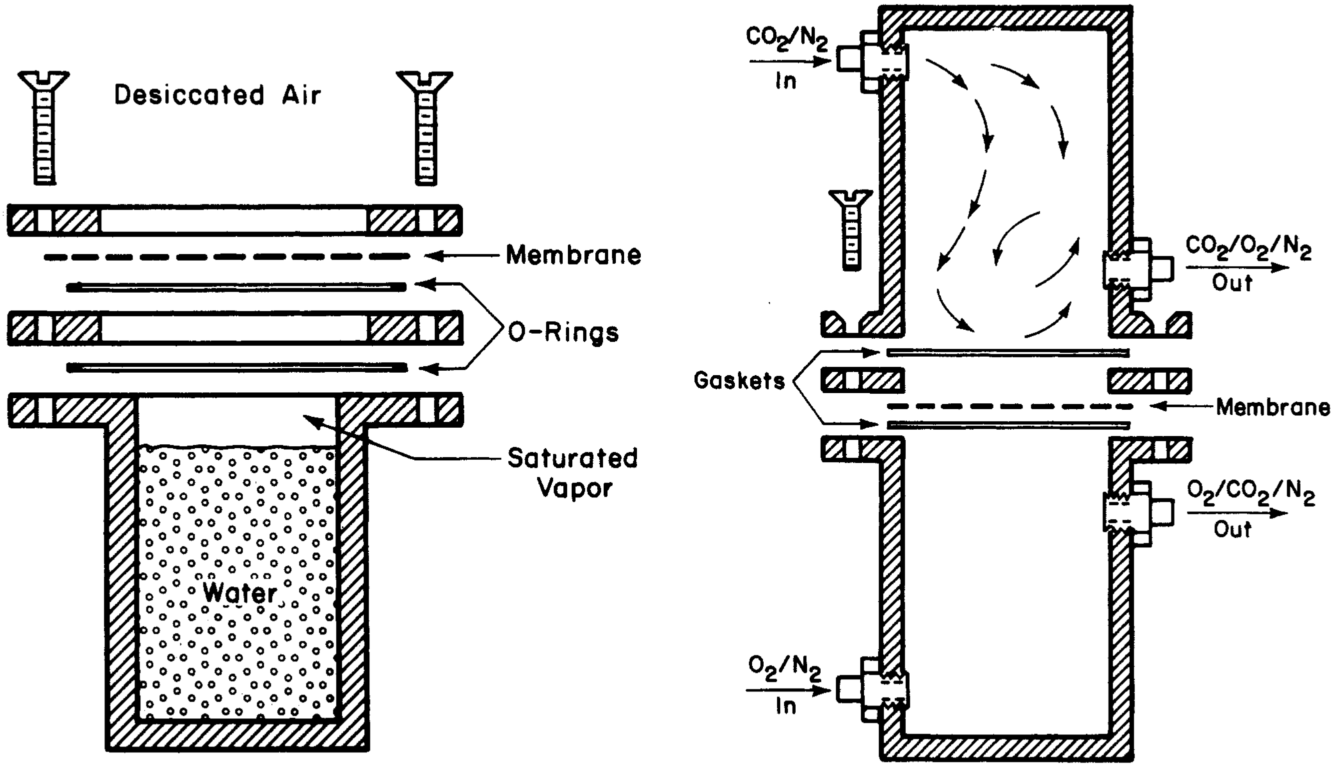
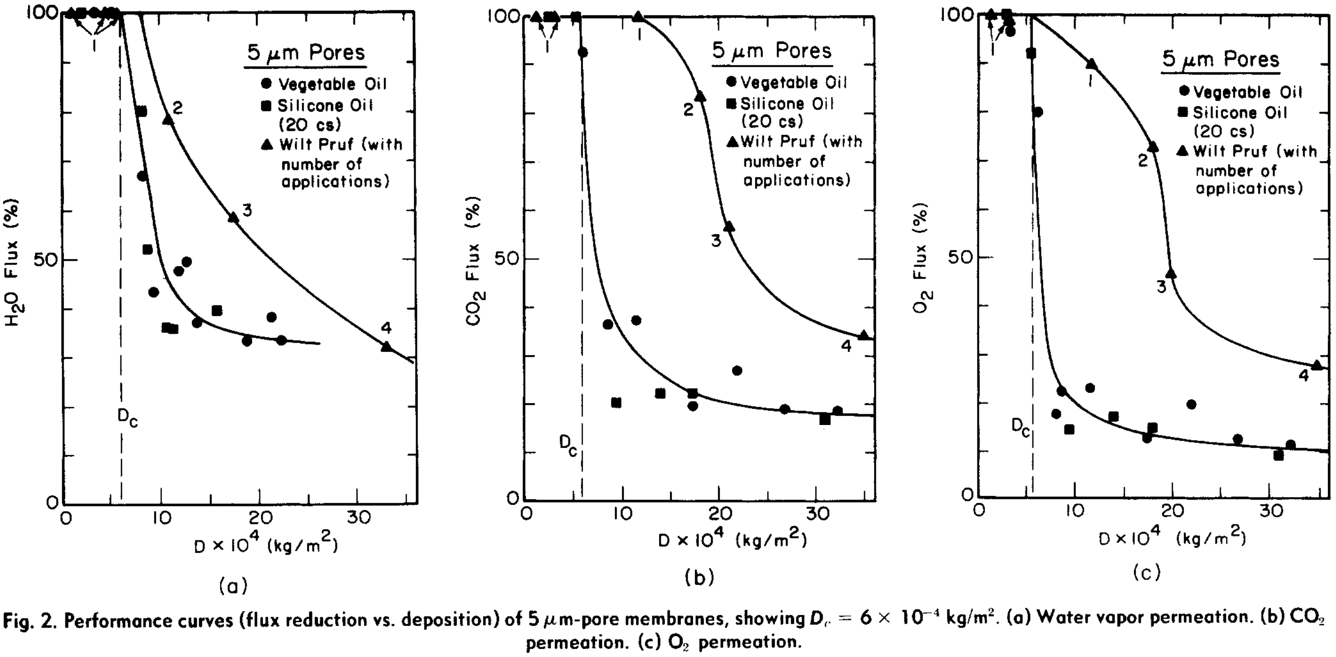


(a) (b)

Figure 1. (a) *Water permeation.* Cell is filled 90% with water, covered with test membrane, and placed in a desiccator. Weighings over several hours determine water loss rate. The open-pore fluxes are comparable to the performance of actual leaf surfaces: the 5-μm pore membrane flux averaged 3 × 10^{-2} kg/m² hr, while the natural range (Meyer *et al.*, 1960) is 5-25 × 10^{-2} kg/m² hr. (b) *CO_2/O_2 permeation.* With the membrane dividing two chambers of the cell, gas streams of standard composition are forced through the chambers at desired rates. The upper stream is 10.1% CO_2 in N_2, the lower stream 5.2% O_2 in N_2, so CO_2 diffuses from the upper chamber to the lower one and O_2 *vice versa*. Flow rates are separately adjusted to assure that both chambers are at the same pressure, so no pressure-driven flow occurs through the pores. Exiting stream compositions are monitored by Beckman infrared CO_2 analyzer and polarographic O_2 analyzer, and entering flow rates are measured by rotameters and controlled by needle valves on the downstream side. Open-pore fluxes for the 5-μm pore membranes averaged 9.0 and 16.7 × 10^{-2} kg/m² hr for O_2 and CO_2, respectively, when bulk flow rates were ~ 0.1 L/min on both sides of the membrane (as they were also for all data shown here).

runs for H_2O permeation in a flow environment yielded results in good agreement with the mass transfer predictions of Keller and Stein (1967). Coatings were normally tested within a day of being deposited. Variations in this delay time did not affect performance; tests over a 4-day period showed no changes in permeability. Performance on real leaves, growing and exposed to sunlight, could be expected to show progressive deterioration after the first day (Anderson and Kreith, 1978).



(a) (b) (c)

Fig. 2. Performance curves (flux reduction vs. deposition) of 5 μm-pore membranes, showing $D_c = 6 \times 10^{-4}$ kg/m². (a) Water vapor permeation. (b) CO_2 permeation. (c) O_2 permeation.

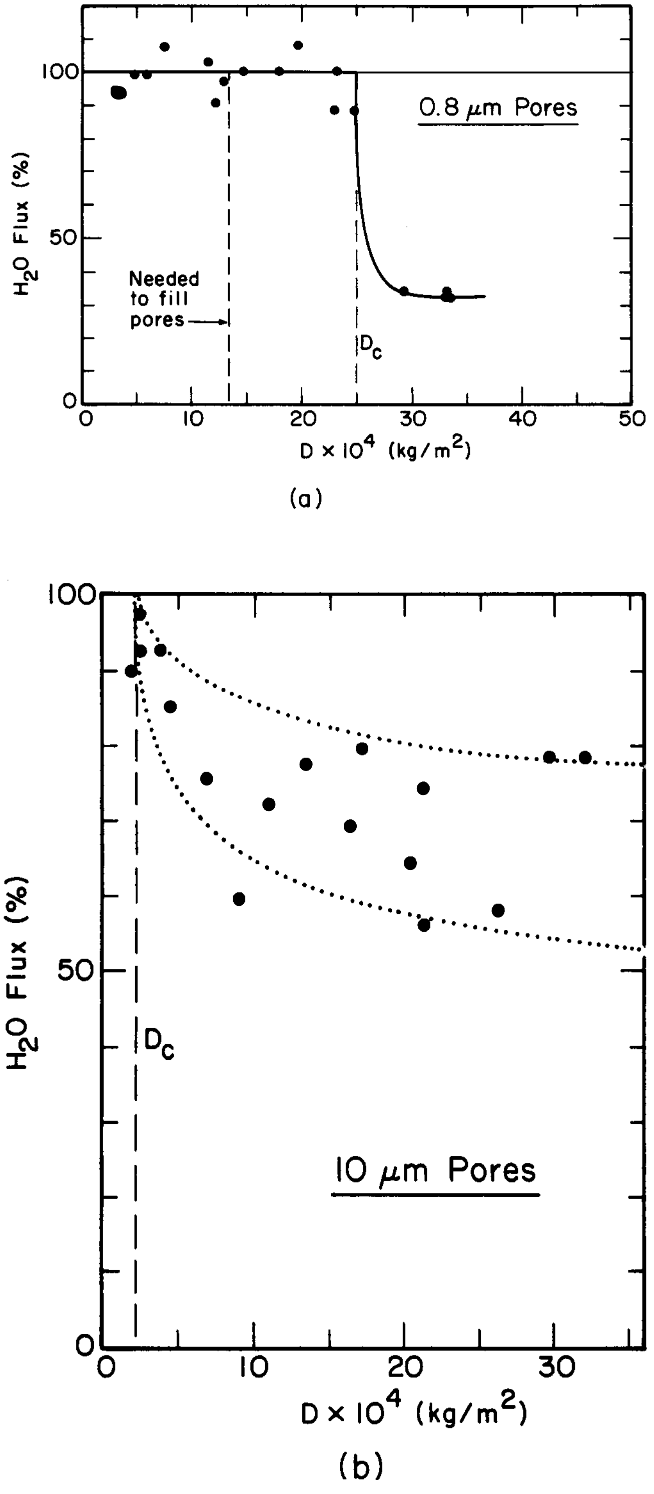


Fig. 3. Performance curves for water vapor permeation with deposition of vegetable oil. (a) 0.8 μm pores, with $D_c = 25 \times 10^{-4}$ kg/m^2. (b) 10 μm pores, with $D_c = 2 \times 10^{-4}$ kg/m^2.

Performance curves, plots of percent flux reduction (relative to uncoated membranes) vs. D, are given for 5 μm pores in Figure 2. A critical threshold value of D, designated D_c, is seen in the range $D \cong 5\text{-}8 \times 10^{-4}$ kg/m^2 in all plots, and to be manifested similarly by silicone and *VO* coatings. The H_2O flux (stagnant) dropped by about 65%, while the CO_2 and O_2 fluxes (convected) dropped by about 80% and 90%, respectively. The greater drop of the latter two is undoubtedly a hydrodynamic effect; in a convected system the relatively smaller boundary layer resistance gives added importance to the resistance offered by pore occlusion. Both silicone and *VO* films were somewhat more permeable to CO_2 than to O_2, but generalizations are hazardous because this experiment involves three-component counterdiffusion with possibly concentration-dependent diffusion coefficients. Nevertheless, real leaves experience the same phenomenon. Wilt Pruf was far less effective than silicone and *VO* as a vapor barrier and exhibited a less dramatic threshold, perhaps because its deposition was sequential rather than continuous.

The existence of a deposition threshold phenomenon has not previously been reported for coatings on any type of porous membrane. Its existence would seem to explain part of previous difficulties with aerosol *AT* delivery (Fisher and Lyon, 1972), since the condition $D < D_c$ would have negligible effect on transpiration. Whereas real leaves have other impediments to *AT* spreading (cuticular hairs, raised guard cells around stomata, etc.) the threshold deposition would still have to be achieved.

To elucidate possible influences of pore diameter, tests were made with *VO* for water permeation with $d = 0.8$ and 10 μm (Figure 3). The smaller pores had a threshold at $D_c \cong 25 \times 10^{-4}$ kg/m^2. Data for the larger pores were not conclusive, but it appears that $D_c \approx 2 \times 10^{-4}$ kg/m^2. Here the large flux reductions seen in Figures 2 and 3a are not achieved and data are far more scattered.

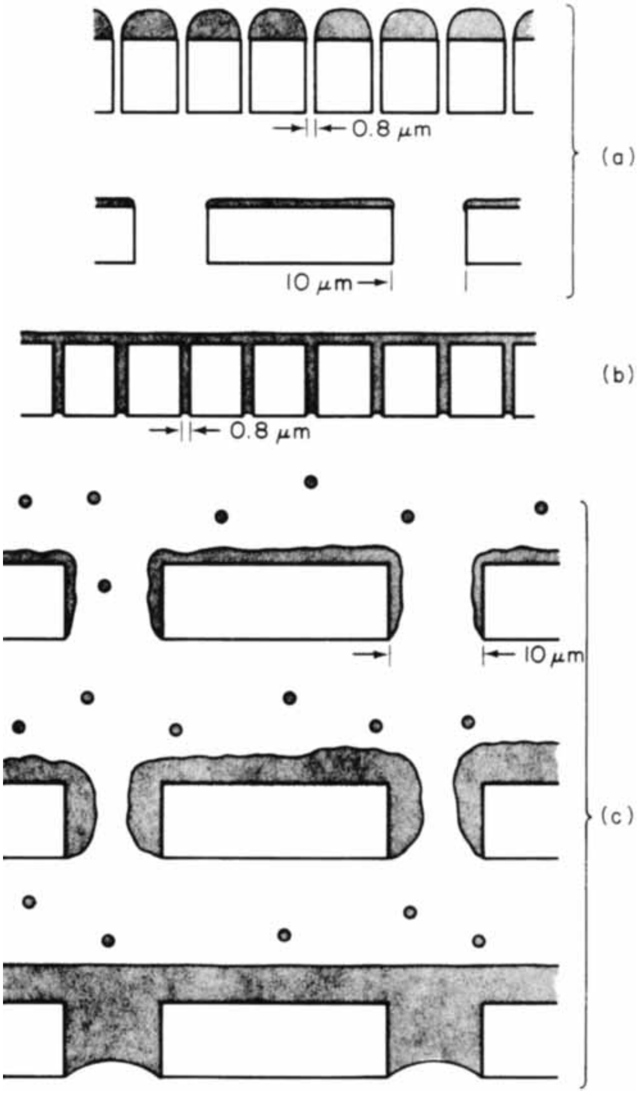


Fig. 4. (a) Membranes with 0.8 and 10 μm pores, at $D \lesssim D_c$ condition. Each drawing is to scale, although the two scales differ slightly. (b) Membrane with 0.8 μm pores when $D \gtrsim D_c$. Occlusion is abrupt and complete. (c) Membrane with 10 μm pores when $D \gtrsim D_c$ (top) and $D > D_c$ (middle) and $D >> D_c$ (bottom). Occlusion is gradual and randomly distributed. Bottoms of filled pores are drawn concave-in to agree with SEM pictures (Erickson, 1978).

In discussing the threshold, we begin by noting that a calculation (Erickson, 1978) of the shape and volume of deposited droplets indicates that coalescence across the *solid* surface must have occurred at D-levels well below D_c in each case—e.g., see Figure 3a. Nonetheless, flux data suggest that fluid failed to enter or cover the pores until $D \gtrsim D_c$. Scanning electron micrographs (Erickson, 1978) also support this conclusion and, moreover, indicate that 5 μm pores were essentially completely full at $D \gtrsim D_c$. One is led, then, to envision cases for $D > D_c$ and $D < D_c$ as drawn schematically for small and large pores in Figure 4. These diagrams help to explain why the 0.8 μm pores would yield an abrupt drop in flux, while with $d = 10$ μm only a gradual flooding of the pores would occur as $D > D_c$. In the latter case, one expects that complete pore conclusion would occur only when $D >> D_c$, and that local occlusion could occur in random fashion so that repeatability would be poor; both these predictions are borne out by Figure 3b.

Despite the qualitative success of this picture, there is still no satisfactory explanation as to why the unexpected threshold at D_c should exist at all. It is, perhaps, worth noting that the product $d \times D_c$ is nearly constant; its value ranges only from 20 to 30×10^{-10} kg/m in Figures 2-3, while d varies 12-fold and D_c 9-fold. This observation has important implications, in general, for the filling of porous surfaces by aerosol liquid deposition. It means that small-pore surfaces (e.g., when plant stomates are small or nearly closed) will be difficult to occlude, and very high D will be necessary to achieve significant flux reduction. In practice, the use of spray droplets larger than d would occlude pores if a direct superposition occurs, but spreading into neighboring pores still might not result. This is probably the case for most agricultural film-forming *AT*'s in the past.

We suggest that further research with *AT* surface chemistry should be productive, inasmuch as D_c is surely sensitive to these properties. It is also likely, because of d-dependence, that successful products and delivery systems may have to be specifically matched to the stomata sizes of individual crops. Finally, as an immediate practical matter, it may be important that *VO* works well as an *AT* and is cheap enough (Erickson, 1978), and its films stable enough, so that it may be directly usable as an environmentally acceptable *AT* at the present time.

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NOTATION

AT = antitranspirant

d = diameter of pore in membrane; μm

D = deposition density of AT on membrane surface (an average); kg/m^2

D_c = critical, or threshold, value of D above which some reduction of transmission of vapor is noted; kg/m^2

VO = vegetable oil

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Secondary Nucleation of Citric Acid due to Fluid Forces in a Couette Flow Crystallizer

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INTRODUCTION

Because of its importance in suspension crystallization processes, much recent effort has been directed toward investigating the phenomenon of secondary nucleation. Recent developments based on the results of single crystal experiments have revealed that secondary nucleation by collision breeding is the dominant nucleation mechanism (Botsaris and Denk, 1972; Strickland-Constable et al., 1969, 1972; McCabe and Coworkers, 1971, 1972; Larson and Bauer, 1974). The methods of the population balance, as formulated by Randolph and Larson

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