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... D. R. Montgomery, 515
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...ation M. E. Eisenhour, 515

... G. M. Bryant

... August 3, 1976

...nating Dept R/D

...ject Proposed Publication on Monomer Removal From PVC Resins

Gentlemen:

Enclosed is a copy of an article, "Phenomenological Studi s of Vinyl Chloride Monomer Removal Fror. Suspension PVC Resin" which is being submitted to the J. of Appl. Po.ym. Sci. for publication. Do you recognize any of the authors, Cheng, Langsam or Mantell as an mployee of one of our competitors? Surprisingly the manuscript do s not identify the authors' industrial or academic association. I do not have a lot of time to review this manuscript, so it will be bri f and sent back soon. If you have any comments you would like to mak conc rning the paper, please let me know within two weeks. Since the manuscript has just arrived and not read, I am not sure that it off rs anything not discussed in the eight or so patents issued on this subject. I am forwarding it on the assumption that it may be helpful to your efforts.

I am also enclosing the summary page of a recent article on th Washburn equation in J. Coll. Int. Sci. The equation was used in the porosimetry-plasticizer work (1969). Since you have recently received your porosimetry you may be interested in this work.

In association with new additions to our staff to work on Enhanced Oil Recovery program, I would appreciate having my surface ch mistry books returned.

With warmest personal regards to all,

Ed

J. E. Glass

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# JOURNAL OF APPLIED POLYMER SCIENCE

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July 28, 1976

Dr. J.E. Glass
Research & Development Dept.
Union Carbode Corp.
Chemicals and Plastics
South Charleston, West Virginia

Dear Sir:

We are enclosing with this letter a manuscript (author and title given below) which has been submitted for publication in the JOURNAL OF APPLIED POLYMER SCIENCE.

We would appreciate receiving your comments on this manuscript and your opinion regarding its suitability for publication in the JOURNAL OF APPLIED POLYMER SCIENCE. Since we are trying to hold the interval between submission and publication dates down to a minimum, I should be very grateful if you could kindly return this manuscript, together with two copies of your comments (one unsigned), to me within the next three weeks. A self-addressed stamped envelope is also enclosed for your convenience.

Very sincerely yours,

H. Mark

H. Mark
Editor

AUTHOR(S): John T. Cheng, Michael Langsam, Gerald J. Mantell

TITLE: PHENOMENOLOGICAL STUDIES OF VINYL CHLORIDE MONOMER REMOVAL FROM SUSPENSION PVC RESIN


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# Rate of Penetration of a Fluid into a Porous Body

## II. Verification of the Generalization of the Washburn Equation, for Organic Liquids in Glass Capillaries[1]

ROBERT J. GOOD AND N. -J. LIN

*Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14214*

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The rate of penetration of a liquid hydrocarbon or an alcohol into a glass capillary is more rapid if the capillary has been outgassed, than if its surface is covered with a duplex film of the liquid. The increase in rate is as large as 10%. If the pore walls are covered by an adsorbed film, the thickness of which is comparable to the pore radius, this leads to an accelerated rate of penetration in comparison to systems in which the pore radii are large. In the systems studied, there was a notable difference between hydrocarbons and octyl alcohol, which appeared when the glass was outgassed at 200°C under vacuum.

### INTRODUCTION

It was recently shown (1, 2) that, for the penetration of a fluid into cylindrical pores of radius $r$, if the pore surfaces are initially not covered with an equilibrium adsorbed film of the penetrating liquid, then the rate of penetration can be faster than that predicted by the Washburn equation (3, 4, 5). In the absence of gravity,

$$\frac{r\gamma_{l_v}\cos\theta_Y}{2\eta} \leq \frac{d(x^2)}{dt} \leq \frac{r}{2\eta} \times (\gamma_{l_v}\cos\theta_Y + \pi_e - \pi_0). \quad [1]$$

Here, $x$ is distance penetrated, $\gamma_{l_v}$ is the liquid–vapor surface tension, $\eta$ is the viscosity, $\theta_Y$ is the equilibrium contact angle, and $\pi$ is the spreading pressure:

$$\pi_e \equiv \gamma_s - \gamma_{s_v}, \quad [2]$$

$$\pi_0 \equiv \gamma_s - \gamma_{s_{(t=0)}}, \quad [3]$$

where $\gamma_s$ is the surface free energy of the solid in the absence of adsorption of molecules of the penetrating liquid, $\gamma_{s_v}$ is the solid surface free energy in equilibrium with the saturated vapor, and $\gamma_{s_{(t=0)}}$ is the solid surface free energy at zero time; $\gamma_s \geqq \gamma_{s_{(t=0)}} \geqq \gamma_{s_v}$. For the systems reported in this paper, the advancing contact angle was indistinguishable from zero. Setting $\theta_Y = 0$, we write

$$\frac{r\gamma_{l_v}}{2\eta} \leq \frac{d(x^2)}{dt} \leq \frac{r}{2\eta}(\gamma_{l_v} + \pi_e - \pi_0) = \frac{r}{2\eta}(\gamma_{s_{(t=0)}} - \gamma_{s_v}). \quad [4]$$

The left equality (which is the Washburn equation) holds provided that the solid surface is covered with a duplex film of the penetrating liquid, or that dissipative transport mechanisms maintain such a film, advancing well ahead

[1] Part of this work was reported at the 48th National Colloid Symposium, Austin, Texas, June, 1974. The fact that the excess driving force for penetration could be expressed in terms of the free energy of immersion was brought out in the open discussion of that paper. If the party who made the suggestion will identify himself to the senior author, due credit will be given in the next paper in this series.



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of the liquid front. An example of a dissipative transport mechanism, which in many cases may proceed rapidly enough to maintain such a film, is evaporation from the liquid, followed by diffusion or flow down a pore, and finally, adsorption or condensation on the walls of the pore. The left relation holds as an inequality if the additional free energy, associated with the wetting of the solid in the absence of a duplex film, can contribute in a nondissipative manner to the *effectual* driving force for flow. The free energy change during flow of a liquid into a cylindrical tube may be identified as the free energy of immersion [6]: If the walls are covered with a film that is in equilibrium with the saturated vapor, we have

$$\Delta G^{i(sat)} = \gamma_{sv} - \gamma_{sl}. \quad [5]$$

If the walls are devoid of adsorbed film, we have

$$\Delta G^{i} = \gamma_{s} - \gamma_{sl}, \quad [6]$$

$$\Delta G^{i} - \Delta G^{i(sat)} = \pi_e. \quad [7]$$

If the walls are initially covered with a film such that the surface free energy is $\gamma_{s(t=0)}$, the free energy change is given by

$$\Delta G^{i0} = \gamma_{s(t=0)} - \gamma_{sl}, \quad [8]$$

$$\Delta G^{i} - \Delta G^{i0} = \pi_0. \quad [9]$$

The purpose of this study was to establish whether appreciable deviations from the Washburn equation, as indicated by Eqs. [1] and [4], are observable.

## THEORY

The following theoretical considerations, beyond those in (2), were developed for the purpose of testing the new equations.

It is quite general to assume that only a fraction, $\alpha$, of the excess driving force, $\pi_e - \pi_0$ in Eqs. [1] and [4], is used in a nondissipative manner. Then, we can write Eq. [4] in the form

$$\frac{d(x^2)}{dt} = \frac{r[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}{2\eta}, \qquad 0 \leq \alpha \leq 1. \quad [10]$$

since deviations from the Washburn equation have not been reported before, it is to be expected that $\alpha$ is commonly small. The maximum conceivable rate would be given by Eq. [10] with $\alpha = 1$.

We have set out to test these equations in perhaps the simplest possible system: vertical glass capillary tubes. Vertical orientation has an advantage over horizontal in that small deviations from horizontal can cause quite appreciable errors. For a vertical tube of radius $r$, the rate, when the meniscus is at height $x$ above the liquid surface, is given by:

$$\frac{dx}{dt} = \frac{r^2}{8\eta x}\left\{\frac{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}{r} - \rho g x\right\}, \quad [11]$$

where $\rho$ is the density of the fluid.

Integrating Eq. [11] between elevations $x_1$ and $x_2$, we obtain

$$t_p = t_2 - t_1 = \frac{8\eta}{\rho g r^2}\left[\frac{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}{\rho g r} \times \ln\left\{\frac{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)] / \rho g r - x_1}{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)] / \rho g r - x_2}\right\} - (x_2 - x_1)\right]. \quad [12]$$

The thickness, $\delta$, of the film on the solid is a variable that was found to be important. It may be assumed that there is some limiting thickness, $\delta_d$ for a duplex film, such that for $\delta < \delta_d$, the vapor pressure of the adsorbed film is appreciably less than the saturation pressure $p_0$; and for $\delta > \delta_d$, the vapor pressure is not experimentally different from $p_0$. We consider, here, only capillary or pore radii in the range large enough that Kelvin equation corrections to the vapor pressure need not be taken into account. For clarity of the qualitative argument regarding $\delta$, we discuss only a horizontal tube (see Fig. 1).

If $\delta_d$ is comparable to the radius $r$, then at saturation, the effective radius will be $r - \delta_d$, with respect to the driving force for pene-