

JOURNAL OF APPLIED POLYMER SCIENCE

Editorial Board: H. Mark, W. Cooper, M. Morton, B. Ranby, P. Weiss

Editorial Office: Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York 11201

July 28, 1976

Dr. J.E. Glass
Research & Development Dept.
Union Carbide 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
Editor

John T. Cheng, Michael Langsam, Gerald J. Mantell

AUTHOR(S):

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 Capillaries¹

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Received February 18, 1974; accepted August 31, 1975

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,

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

Here, x is distance penetrated, γ_{lv} is the liquid-vapor surface tension, η is the viscosity, θ_Y is the equilibrium contact angle, and π is the

spreading pressure:

$$\pi_s = \gamma_s - \gamma_{ss}, \quad [2]$$

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

where γ_s is the surface free energy of the solid in the absence of adsorption of molecules of the penetrating liquid, γ_{ss} 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; $\gamma_s \geq \gamma_{s(t=0)} \geq \gamma_{ss}$. For the systems reported in this paper, the advancing contact angle was indistinguishable from zero. Setting $\theta_Y = 0$, we write

$$\begin{aligned} \frac{r\gamma_{lv}}{2\eta} \leq \frac{d(x^2)}{dt} &\leq \frac{r}{2\eta} (\gamma_{lv} + \pi_s - \pi_0) \\ &= \frac{r}{2\eta} (\gamma_{s(t=0)} - \gamma_{ss}). \quad [4] \end{aligned}$$

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

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

If the walls are devoid of adsorbed film, we have

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

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

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, α , of the excess driving force, $\pi_s - \pi_0$ in Eqs. [1] and [4], is used in a nondissipative manner. Then, we can write Eq. [4] in the form

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

Since deviations from the Washburn equation have not been reported before, it is to be expected that α 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:

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

where ρ is the density of the fluid.

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

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

The thickness, δ , 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, δ_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 δ , we discuss only a horizontal tube (see Fig. 1).

If δ_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-

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Date: July 28, 1976

Author: John T. Cheng, Michael Langsam, Gerald J. Mantell

Title: phenomenological studies of vinyl chloride monomer removal
from suspension pvc resin

Is this paper acceptable for publication in the Journal of Applied Polymer Science?

(1) YES ☐ (2) With minor revision ☐ (3) With major revision ☐

(4) NO ☒ If not, do you suggest another journal Possibly in Chemical Engineering Progress
based on current interest, not technical merit.

COMMENTS:

The statements, "there are complications in this study because the apparent porosity correlation is based on the assumption" and "we have not yet examined the effect of glassy particles in a systematic manner" define in the authors' own words part of the deficiencies in this manuscript. The study examines only four resins which vary so extensively in particle size distribution (one bimodal and another excessively high in fines) and glassy particle characteristics that no definitive conclusion can be made about the mechanism(s) of vinyl chloride monomer removal. Characterization and interpretation of the particle's porosity and glassiness by the IPTU and density tests are questionable even when such measurements are applied to a series of resins with only minor variations in properties. The tests are totally inadequate in supporting the authors' preconceived ideas on the mechanism(s) of monomer removal.

Amen!
The authors should re-evaluate the merits of the submitted manuscript with respect to their previous publication and the disclosures in numerous patents on the subject of monomer removal, e.g. NL 7,507,385, BE 830,689, NL 7,507,527, DT 2,429,776, U.S. 3,926,927 and DT 2,451,988. It is difficult for this reviewer to find any novel or contributive value in the submitted paper.

There are several minor inconsistencies and inaccuracies in the manuscript. For example, the first three parameters in Section B approximately define the limits of the added solvent's solubility parameter; therefore, it is not a required fourth parameter, by definition. In Section C, diluting the slurry with increased amounts of water does not change the polymer to water interfacial area, etc.

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