JOURNAL OF APPLIED POLYMER SCIENCE VOL. 18, PP. 1655-1662 (1974)

Absorption of Cyclohexane on a Poly(tetrafluoroethylene) Surface

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Synopsis

Heat transfer measurements made when cyclohexane condenses on poly(tetrafluoroethylene) provide further support to the theory that absorption can occur on this surface.

INTRODUCTION

A number of papers have been published recently describing surface phenomena on poly(tetrafluoroethylene) which support the idea that absorption can take place on this surface. Neumann et al.[1] have described the temperature dependence of the contact angles of alkanes ranging from *n*-decane to hexadecane at 25–70°C and showed that the first three members of the series, i.e., *n*-decane, *n*-undecane, and *n*-dodecane exhibited finite temperature coefficients, although no effect of temperature was observed for the remaining hydrocarbons. They concluded that absorption took place on the poly(tetrafluoroethylene) since Whalen and Wade[2] have shown that no adsorption of long-chained alkanes would occur.

The conjecture of absorption occurring had been previously propounded by Graham.[3] Boyes and Ponter,[4] when measuring the contact angles of cyclohexane under condensation conditions at 72–774 torr pressure on this surface, also showed that the contact angles decreased from 15° to 0°, which was attributed to absorption which resulted in an increase in the solid–vapor interfacial free energy. It is interesting to assess the influence of this permeation on the physical properties of the poly(tetrafluoroethylene), and the following work describes a preliminary investigation to evaluate the thermal conductivity of poly(tetrafluoroethylene) in an environment of cyclohexane.

EXPERIMENTAL

The condensation heat transfer rates using pure cyclohexane and a number of other organic vapors, including benzene, carbon tetrachloride, and 1,1,2-trichloroethylene, were measured using an apparatus shown in Figure 1, which consisted essentially of a single 1-in.-diameter horizontal

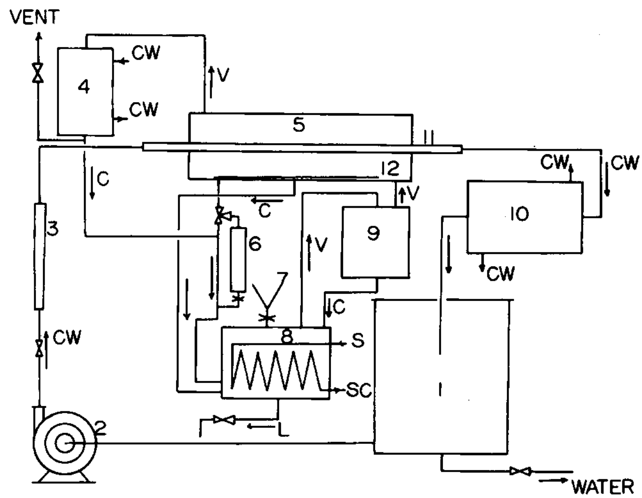

Fig. 1. Schematic flow diagram of equipment: (1) cooling water reservoir; (2) "Chem-Gard Vanton" centrifugal pump; (3) rotameter for measuring cooling water flow rate; (4) secondary condenser; (5) test condenser; (6) calibrated separatory funnel for measuring condensation rate; (7) charging funnel; (8) boiler; (9) vapor entrainment separator; (10) heat exchanger; (11) condenser tube; (12) trough; (L) liquid; (C) condensate; (V) vapor; (S) steam; (CW) cooling water; (SC) steam condensate.

tube, either copper or copper coated with the poly(tetrafluoroethylene) to an average thickness of 0.00135 in., on which the vapors condensed. Twelve thermocouples (33 gauge, copper–Constantan) were imbedded in the condenser tube wall with low-expansion cement. The details of thermocouple installation are given in Figure 2.

The wall was polished with emery paper until the surface was smooth, and the tube was thoroughly washed with acetone and methanol before placing it in the condenser chest. The condenser tube surface was oxidized by using it as a steam condenser. Initially, the steam condensed in a dropwise manner on the polished surface, but changed slowly to a filmwise mode of condensation and after about 30 operating days consistently produced filmwise condensation. After completing the experimental work with the oxidized copper tube, the tube was removed from the test condenser and thoroughly washed with acetone and methanol. It was then coated with poly(tetrafluoroethylene) (chemically pure grade) spray, by placing the tube in a lathe and slowly rotating while impinging the tube with the spray in a traverse at constant speed. Three successive coatings were applied, and it was shown that very even distribution of the film resulted.

The coated tube was cured for 48 hr in an oven maintained at 200°F, to ensure that no aerosol was occluded; and the resulting poly(tetrafluoroethylene) film was found to adhere strongly to the black oxide film. After 20 weeks of continuous condensation, no deterioration of the film could be observed. The experimental work was repeated using the poly-

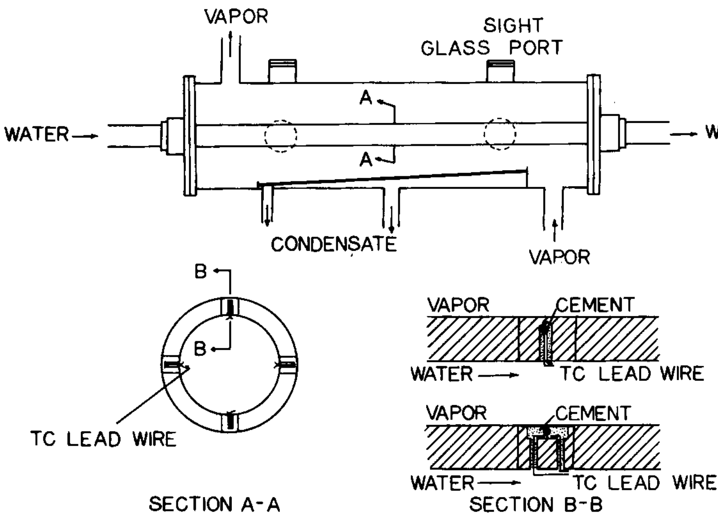

Fig. 2. Test condenser and thermocouple details.

(tetrafluoroethylene)-coated copper tube. The thickness of the poly-tetrafluoroethylene) coating was found by measuring the diameter of the tube before and after the coating with a micrometer; an average of 35 measurements gave a value of 0.00135 in. Heat transfer rates were measured using both surfaces.

DISCUSSION

Plots of condensation heat transfer rates Q' versus the difference between the saturation temperature and the inside copper surface temperature ΔT for the systems benzene, cyclohexane, and 1,1,2-trichloroethylene condensing on both the horizontal copper and the coated tubes are given in Figures 3–5. It has been established that the mode of condensation is filmwise for these systems.[5,6] The heat transfer resistance exhibited by the cyclohexane on the coated tube is larger than that using the benzene and trichloroethylene systems. By assuming that the heat transfer through the condensate film is by conduction alone, it can be shown that the heat conducted through the condensate film and a poly(tetrafluoroethylene)-coated copper surface is given (Fig. 6) by

$$Q = \frac{(T_s - T_{c'}) \times 2\pi L}{\left[\dfrac{\ln\dfrac{r_5}{r_4}}{k_{\text{liquid}}} + \dfrac{\ln\dfrac{r_4}{r_2}}{k_{\text{P.T.F.E.}}} + \dfrac{\ln\dfrac{r_2}{r_1}}{k_{\text{copper}}}\right]} \tag{1}$$

where k = thermal conductivity.

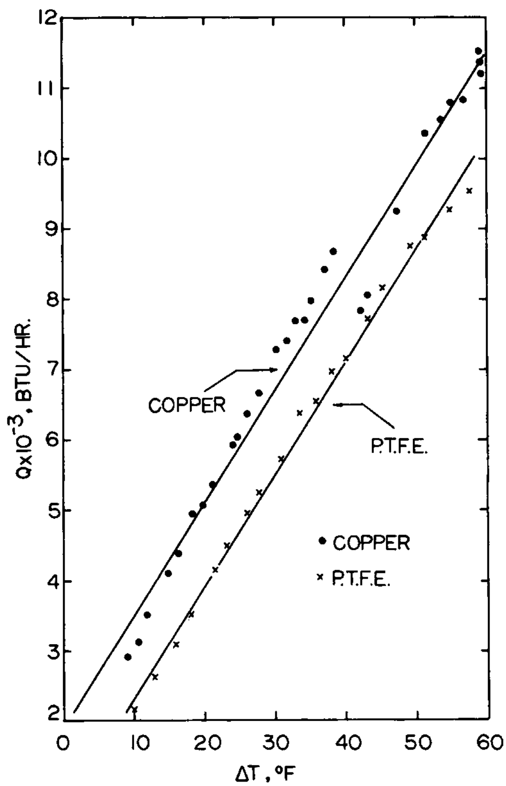

Fig. 3. Heat transfer rates for pure benzene condensing on copper and P.T.F.E.-coated copper surfaces.

Similarly, the heat conducted through the condensate film and the uncoated copper tube is given by

$$Q = \frac{(T_s - T_c) \times 2\pi L}{\left[\frac{\ln\frac{r_3}{r_2}}{k_{\text{liquid}}} + \frac{\ln\frac{r_2}{r_1}}{k_{\text{copper}}}\right]}. \tag{2}$$

Letting $T_5 - T_{c'} = \Delta T_{c'}$ and $T_5 - T_c = \Delta T_c$, then from eqs. (1) and (2) for the same value of Q

$$\Delta T_{c'} - \Delta T_c = \frac{Q}{2\pi L}\left[\frac{\ln\frac{r_5}{r_4}}{k_{\text{liquid}}} - \frac{\ln\frac{r_3}{r_2}}{k_{\text{liquid}}} + \frac{\ln\frac{r_4}{r_2}}{k_{\text{P.T.F.E.}}}\right]. \tag{3}$$

Since the thickness of the poly(tetrafluoroethylene) layer is small compared with the radius of the copper tube, i.e., $r_4 \simeq r_2$ and $r_5 \simeq r_3$, and equation (3) may be rewritten as

$$\Delta T_{c'} - \Delta T_c = \frac{Q}{2\pi L} \times C$$

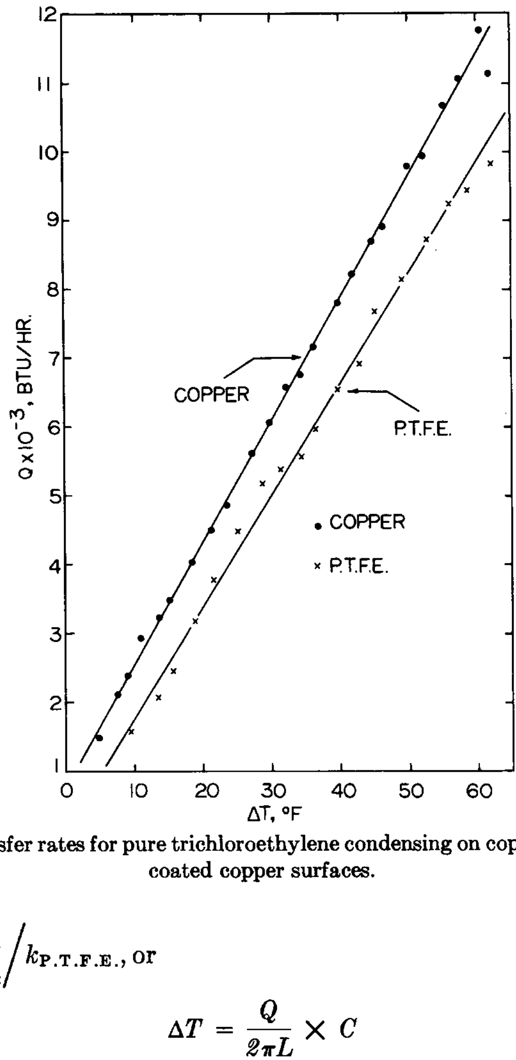

Fig. 4. Heat transfer rates for pure trichloroethylene condensing on copper and P.T.F.E.-coated copper surfaces.

where $C = \ln\frac{r_4}{r_2} \Big/ k_{\text{P.T.F.E.}}$, or

$$\Delta T = \frac{Q}{2\pi L} \times C \tag{4}$$

where $\Delta T = \Delta T_{c'} - \Delta T_c$, the thermal conductivity of the poly(tetrafluoroethylene) layer exposed to the cyclohexane can be determined from eq. (4). Poly(tetrafluoroethylene) exhibits two crystalline transitions at 19°C and 30°C, and the X-ray data of Bunn and Howells[7] have shown that below the 19°C transition, an orderly triclinic lattice molecular arrangement exists, while above 19°C there is some disorder which was attributed to either rotation or translation of the molecules with respect to their long axes. Pierce et al.[8] demonstrated that the helical molecule untwists slightly during the 19°C transition and that the molecular packing changes from an ordered triclinic arrangement to a partially disordered structure with an hexagonal unit cell. At all temperature below the melting point the disorder is limited to types which do not disturb the periodic

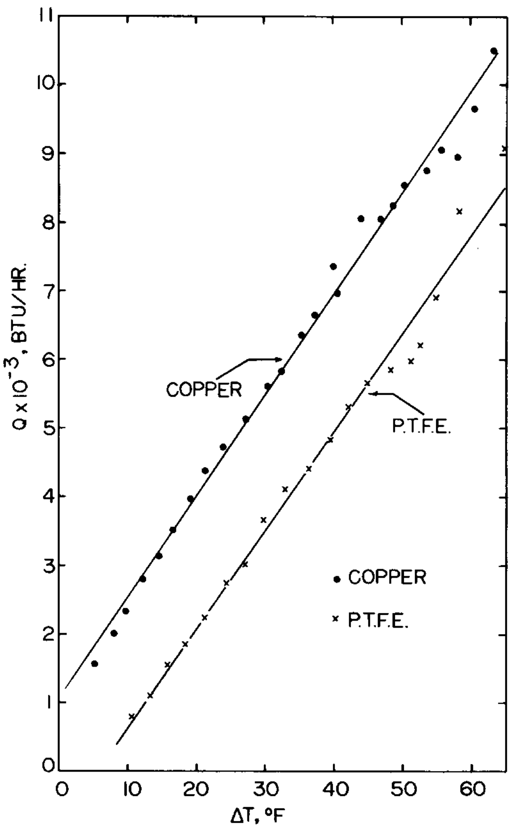

Fig. 5. Heat transfer rates for pure cyclohexane condensing on copper and P.T.F.E.-coated copper surfaces.

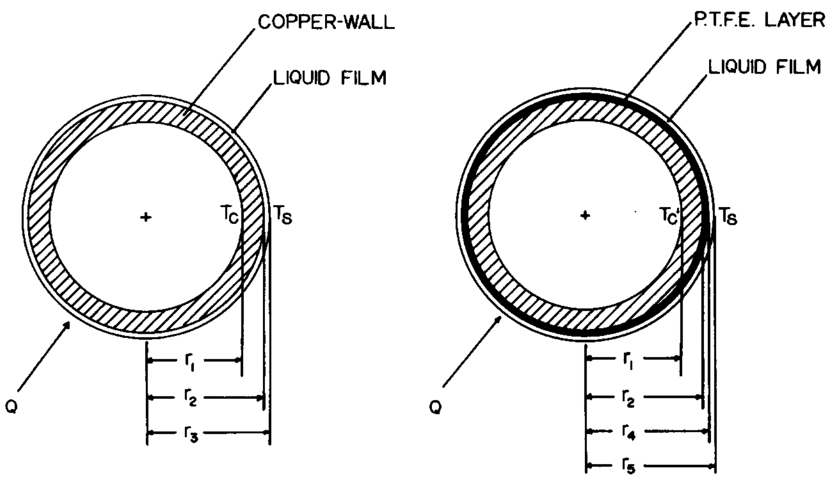

Fig. 6. Filmwise condensation on copper and P.T.F.E.-coated copper tubes.

TABLE I
Influence of P.T.F.E. Film Temperature on Conductivity in Presence of Cyclohexane

Q, Btu/hr	k, Btu/(hr)(ft²)(°F/ft)
2000	0.0241
3000	0.0348
4000	0.0482
5000	0.0580
6000	0.0709
7000	0.0782
8000	0.0894

placement of the long axes of the molecules, and the molecules in lateral direction are assumed to remain in regular hexagonal packing.

From nuclear magnetic resonance measurements, Hyndman and Origlio[9] have concluded that the angular displacements of the chain molecules result from motion of the molecules, while Clark and Muus[10] have presented a mechanism for crystal disordering in terms of uncoiling of the chain together with torsional oscillation of molecular segments. The increased heat transfer resistance now described is attributed to absorption into the poly(tetrafluoroethylene) where it is suggested that the cyclohexane exhibits molecular orientation resulting in an anisotropy in the thermal conduction component required for heat transfer. From the above result, it can be shown that the thermal conductivity of the impregnated poly(tetrafluoroethylene) is dependent upon the heat flow through the solid, as shown in Table I. This is in contrast to the bulk value of cyclohexane of 0.066 Btu/(hr) (ft^2) (°F/ft) and the poly(tetrafluoroethylene) value of 0.14 Btu/(hr) (ft^2) (°F/ft). In previous work, Sutherland et al.[11] had suggested that the molecular orientation decreased the thermal conductivity values for octadecane, while Ziebland and Patient[12] later, using more sophisticated measurements, found the reverse. At this time, therefore, a more definite attempt to attribute the increased heat transfer resistance cannot be made.

Nomenclature

- k_{copper} — thermal conductivity of copper condenser tube, Btu/(hr)(ft^2)(°F/ft)
- k_{liquid} — thermal conductivity of liquid film, Btu/(hr)(ft^2)(°F/ft)
- $k_{P.T.F.E.}$ — thermal conductivity of poly(tetrafluoroethylene) coating on condenser tube, Btu/(hr)(ft^2)(°F/ft)
- L — condenser tube length, ft
- Q — heat transfer rate, Btu/hr
- r — radii, as indicated in Figure 6
- ΔT — difference between the saturation or condensation temperature (T_s) and the inside surface of the condenser tube temperature (T_c or T_c'), °F.

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Received June 8, 1973
Revised October 30, 1973