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THE EXPERIMENTAL DETERMINATION OF WALL-FLUID MASS TRANSFER COEFFICIENTS USING PLASTICIZED POLYMER SURFACE COATINGS

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Abstract—A novel profilometric technique for determining local mass transfer coefficients at solid surfaces is described, and the conditions for its successful and advantageous practical application are deduced from basic principles.

Instead of the volatile or soluble surface coatings customarily employed in profilometric work, the coatings used in the method described here are composed of involatile polymer capable of absorbing volatile or soluble swelling agents. Rates of transfer of swelling agent to or from the surface by the experimental fluid stream can then be deduced from measurements of the swelling or shrinking rate of the coating. This system has the advantage that the coating itself does not require frequent renewal; for each fresh experiment it can be re-activated by discharge of accumulated swelling agent or by re-immersion in the swelling bath. A further advantage is the ease with which the Schmidt number can be varied; this can be accomplished by a change of swelling agent alone, without change of experimental fluid or polymer coating. Moreover, this technique offers the possibility of investigating wall-wall mass transfer situations, which cannot readily be studied by conventional means.

In a general analysis of the case in which the coating is initially charged with swelling agent, it is shown how suitable polymer-swelling agent systems and operating conditions may in practice be chosen so that local rates of coating shrinkage are an accurate measure of local fluid-side mass transfer coefficients. Essential data are given for a practical coating system, which is shown to behave as the analysis predicts.

NOMENCLATURE

C,	concentration of swelling agent at some designated point in the swollen polymer;
C_m,	thickness-averaged instantaneous concentration of swelling agent in polymer coating;
C_{1m}, C_{2m},	initial and final thickness-averaged values of C for coating;
ΔC_m,	change in thickness-averaged concentration;
C_0,	initial uniform bulk or average concentration of swelling agent in polymer coating;
C_s,	concentration of swelling agent in the surface of the swollen polymer;
c_s,	concentration of swelling agent in fluid in equilibrium with swollen polymer of surface concentration C_s;
D,	diffusivity of swelling agent within swollen polymer coating;
D_g,	diffusivity of swelling agent in air;
d,	hydraulic diameter of channel, $= d_2 - d_1$ for annulus;
d_1,	inner diameter of annulus;
d_2,	outer diameter of annulus;
F_s,	mass flux of swelling agent across polymer/fluid interface;
f_1,	function of ϕ_1 and χ represented in Fig. 1;
f_2,	function of $F_s\delta_1/\rho D$ and δ'/δ_1 defined by equation (10);
f_3,	function of f_2 defined by equation (11);

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f_4,	a function defined as $(\delta_1/\delta' - 1)f_1$;
k,	mass transfer coefficient at solid-fluid interface, $\equiv F_{s/c_s}$ when the experimental fluid is free of swelling agent;
M,	molecular wt. of swelling agent;
m,	mass of swelling agent present in coating per unit superficial area of coating;
n,	positive integer occurring in equation (3);
p_0,	equilibrium vapour pressure of pure swelling agent;
p_s,	vapour pressure of swelling agent above swollen polymer at equilibrium;
Q,	lateral flux of swelling agent within polymer film in x direction (i.e. parallel to surface), averaged over film thickness, δ;
q_y,	lateral flux of swelling agent within polymer film in x direction at distance y from film-substrate boundary;
R,	gas constant;
T,	absolute temperature;
t,	elapsed time from commencement of transfer;
t',	maximum allowable duration of an experiment, in which ϕ at a point in the surface of the swollen film changes by $(\phi_1 - \phi_2)_s$;
u,	cup-mean velocity of air in annular channel;
v_1, v_2,	initial and final total volumes of sample of swollen polymer containing volume v_R of dry polymer;
v_R,	volume of dry polymer in sample of swollen material;
v_{s_1}, v_{s_2},	initial and final volumes of swelling agent associated with volume v_R of dry polymer;
Δv,	change in volume of swollen polymer sample upon transfer of swelling agent;
x,	distance measured laterally, i.e. parallel to film surfaces;
x_1,	streamwise distance from commencement of transferring section;
$\bar{x}$,	$\dfrac{x_1}{d\,.\,Re\,Sc}$;
$\bar{x}'$,	$\dfrac{x_1}{d\,.\,Re\,Pr}$;
y,	distance from film-substrate boundary;
δ,	thickness of polymer surface coating;
$\Delta\delta$,	change of coating thickness;
δ_1, δ_2,	initial and final values of δ corresponding to t';
δ,	maximum allowable recession of surface coating, corresponding to t', $= \delta_1 - \delta_2$;
v,	kinematic viscosity of air;
ρ,	density of pure swelling agent;
ϕ,	volume fraction of swelling agent in swollen polymer;
ϕ_1, ϕ_2,	initial and final values of ϕ at a given region of the film in an experiment in which c_s or p_s at the same region changes by the allowable fraction (5 per cent);
$(\phi_1 - \phi_2)$,	difference between initial and final values of ϕ at a point in the surface of the swollen film in an experiment in which p_s at the same point changes by the allowable fraction, $\equiv f_1$;
ϕ_{1m}, ϕ_{2m},	initial and final thickness-averaged values of ϕ for coating;
χ,	constant for polymer/swelling agent system, characterizing the degree of interaction between the components;
Nu,	Nusselt number for heat transfer,
Pr,	Prandtl number for fluid flowing in annular channel;
Re,	Reynolds number for flow in annulus, $= ud/v$;

Sc,	Schmidt number for swelling agent/air system; $= \nu/D_g$;
Sh,	Sherwood number for mass transfer, $= kd/D_g$.

INTRODUCTION

THE AIM of the analysis and experiments described here was to establish the validity and proper operating conditions of a novel type of profilometric method for determining mass transfer rates at solid surfaces—an experimental method more convenient and flexible than the solid-sublimation or dissolution techniques in common use. The essence of the new technique is that the solid surface of interest is composed of an involatile or insoluble polymer, which can be swollen in a reversible manner by a volatile or soluble plasticizer or swelling agent. Transfer of this swelling agent to or from the polymer surface by the experimental fluid stream results in (local) changes in the degree of swelling. It will be shown that the conditions can be so chosen that the dimensional changes occurring over a known time provide an accurate measure of the local fluid-side mass transfer coefficients over the surface.

The new technique was conceived by the present authors as likely to offer the following practical advantages over more conventional profilometric methods:

1. The transferring polymer surface, unlike that of a subliming or soluble solid, need be fabricated only once for any number of mass-transfer experiments.
2. A variety of swelling agents, having a wide range of physical properties, is available for a given polymer. It is thus possible to vary the Schmidt number over a substantial range without change of experimental fluid.
3. Since the polymer surfaces can either absorb or desorb swelling agent, polymer–plasticizer systems can be made in which the transfer is from one wall to another across an intervening stratum of fluid. It is thus possible to model exactly the important class of wall-wall heat (and momentum) transfer problems, preserving similarity of flux distribution and of boundary conditions in a way not readily accomplished in conventional mass transfer systems. [1]

We here establish theoretically the conditions under which, in particular, local gas-side mass transfer coefficients may be accurately estimated from measurements of the changes of thickness of plasticized polymeric surface coatings swollen with volatile plasticizers. We further show that these conditions can be attained in practical cases, and report experimental demonstrations of the soundness of the method. Finally, we report data for a practical coating system, for which absolute values of transfer coefficients to air can accordingly be determined from measurements of rate of recession.

An application in which the expected advantages of the method have been realized and exploited in the determination of new mass transfer data has been noted previously [2] and others will be described in subsequent papers.

PRELIMINARY CONSIDERATIONS

As indicated above, it is desirable that the coating can be repeatedly swollen and shrunk without suffering irreversible changes. Rubber coatings can have this property, as they are chemically inert towards many reagents that swell them strongly and are sufficiently deformable to swell and shrink without cracking.

In the case of a thin soft rubber surface coating, which though deformable is virtually incompressible, and for which the superficial area is maintained nearly constant by adhesion to the rigid substrate as swelling proceeds, it is reasonable to assume that local changes of coating thickness are proportional to local volumetric changes. Furthermore, changes in the volume fraction of swelling agent in such a coating are related to changes in the equilibrium concentration or vapour pressure over its surface in the same way as for an unconfined sample of rubber, since compressive stresses are negligible and shearing stresses have no effect on the equilibrium [3]. These considerations apply, of course, whether the transferring stream is liquid or gaseous.

GENERAL CONDITIONS GOVERNING THE APPLICABILITY OF THE METHOD TO THE DETERMINATION OF TRANSFER COEFFICIENTS TO AIR

The rates of recession at different points on the surface of a coating losing volatile material to an air-stream are proportional to the different air-side 'film' coefficients of mass transfer at these points if, and only if, the following conditions hold over the period of measurement:

A. diminution of thickness is proportional to mass of swelling agent transferred;

B. the effective vapour pressure of the swelling agent over the surface is everywhere the same initially, and remains sensibly constant as the transfer proceeds;

C. the overall resistance to mass transfer is predominantly in the gas phase;

D. the behaviour of the coating at any given point is governed only by the local situation, and is not significantly affected by lateral diffusion or differential stress effects.

If the coating is uneven, it is further necessary that:

E. the relationship between mass transfer and shrinkage rate should be uniform over all parts of the polymer layer, in spite of any inequalities in the original coating thickness.

These requirements, and the conditions for their practical fulfilment, will now be examined in turn.

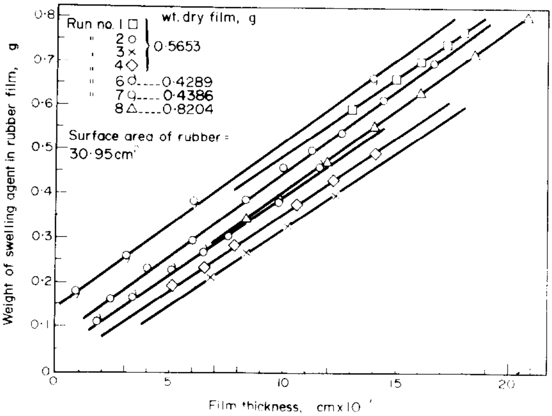

FIG. 1. Weight of swelling agent in various coating specimens plotted against measured coating thickness.

A. *Constancy of volume–composition relationship for swollen polymers*

Rubbers and many of their solvents and swelling agents, having virtually zero heats of mixing [4], show no total volume change on swelling. The consequent proportionality of coating thickness change to mass transferred is demonstrated for natural latex/methyl salicylate systems over a composition range much exceeding that of present practical interest by the results recorded in Fig. 1. This figure shows change of coating-thickness plotted against weight loss in transfer to air flows for coagulant-dipped natural latex coatings swollen with methyl salicylate to various degrees. The relationships show no significant deviation from linearity, and the slopes of the lines, though differing among themselves by about ±4 per cent from their mean, show no significant correlation with initial coating thickness or degree of swelling. The coating density, moreover, remains nearly constant. The apparatus used in these experiments is shown in Fig. 2 and is described in detail in [5]. A long cylindrical rod, coated with swollen films of various thicknesses, was exposed to an axial stream of air at an adjustable and measured flow rate in a coaxial tube of larger diameter. Coating thickness changes were measured at known time intervals by means of the combined pneumatic and electromagnetic gauge described in [6], and the corresponding weight losses were found by weighing a removable section of the rod.

To the extent that the total volume is constant, it is noteworthy that the volume shrinkage is necessarily directly proportional to the total mass of swelling agent transferred, irrespective of any variation of concentration with depth within the polymer layer.

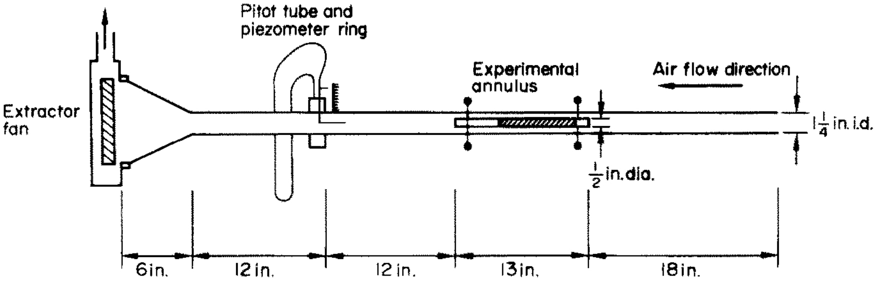

FIG. 2. Apparatus used in the determination of thickness changes and weight losses for a coating at the inner wall of an annular air-duct.

B. *Vapour pressure–composition relationships for swollen coatings.*

Inasmuch as the plasticized polymer constitutes a single phase, a system in which the swollen coating is in equilibrium with vapour of the swelling agent comprises two components and two phases and thus, according to the Phase Rule, has two degrees of freedom. It follows that the vapour pressure of the swelling agent over the surface depends both on temperature and on the composition of the coating, and must in principle change as volatilization proceeds at constant temperature. However, by suitable choice of conditions this change of vapour pressure consequent upon a measurable transfer of swelling agent may in practice be kept within very small limits, as will now be shown.

The relation between the vapour pressure of the swelling agent and the composition of unvulcanized swollen rubber in equilibrium with it is described [7, 8] by the Flory–Huggins equation [9], whose form is deducible from statistical thermodynamical considerations. For a polymer of very high molecular weight this equation reduces to:

$$\log_e (p_s/p_0) = \log_e \phi + 1 - \phi + \chi(1 - \phi)^2 \quad (1)$$

—where ϕ is the volume fraction of swelling agent in the swollen polymer above which the equilibrium vapour pressure is p_s, and p_0 is the vapour pressure of the pure swelling agent at the same temperature.* χ is a constant, characteristic of the polymer-plasticizer system under consideration.

It is reasonable to assume that a progressive change in p_s of up to 5 per cent during an experiment has a negligible effect on the determination of mass transfer coefficients compared with other sources of error. The change in ϕ, $\phi_1 - \phi_2$, corresponding to this 5 per cent change in vapour pressure above the polymer, can be found by solving the following equation derived from equation (1)

$$\log_e \frac{\phi_2}{\phi_1} = \log_e 0{\cdot}95 + (\phi_2 - \phi_1) \times (1 + \chi(2 - \phi_1 - \phi_2)). \quad (2)$$

Computed solutions of equation (2) are represented in Fig. 3 by plots of $(\phi_1 - \phi_2) = f_1(\phi_1, \chi)$.

Now the rate of transfer of swelling agent from the coating to a steady stream of pure air is proportional to the partial pressure of the vapour over the coating surface, with which the immediately adjacent stratum of fluid can be assumed always to be in equilibrium. While p_s remains within 5 per cent of its initial value,

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* Cross-linked systems, and hence vulcanized rubbers, are more accurately described by the Flory–Rehner equation, containing an additional term. For soft vulcanized rubbers, however, the cross-links are infrequent and the extra term is negligible. The correction is also negligible when the rubber is swollen nearly to equilibrium, i.e. when $p_s \simeq p_0$.

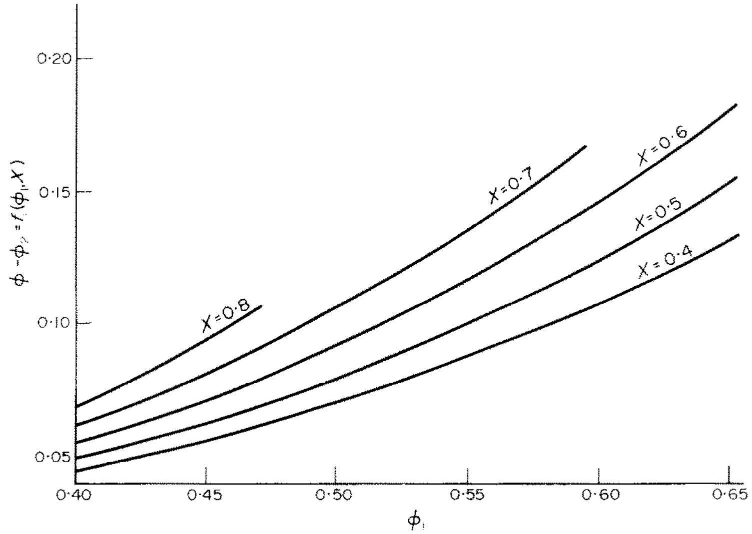

FIG. 3. $f_1(=\phi_1-\phi_2)$, the change in volume fraction of swelling agent in a swollen polymer corresponding to a 5 per cent change in equilibrium vapour pressure, plotted as a function of ϕ_1, the initial volume fraction of swelling agent, and χ the interaction factor in the Flory–Huggins equation describing the equilibrium. (Curves for which $\chi > 0{\cdot}5$ terminate at values of $\phi_1 < 1$ corresponding to the magnitude of the equilibrium swelling. The latter decreases with increasing χ.)

therefore, the transfer rate can be assumed constant for practical purposes. When ϕ_2 at the coating surface falls below the value given by equation (2), however, the rate of transfer declines significantly and is now controlled increasingly by the diffusional properties of the surface coating, which are concentration dependent and generally unknown. Only during the 'constant rate' period, therefore, can the system be used for determining air-side mass transfer coefficients.

The following analysis of the behaviour of a swollen coating shrinking during transfer is artificially simplified by the assumption of a constant diffusion coefficient in the rubber phase. It is nevertheless useful for the limited purpose of determining the extent and duration of the 'constant rate' behaviour.

For a plane sheet of fixed thickness δ and uniform diffusivity D, having initially a uniform concentration C_0 of transferring material, impermeable at one face and subject at the other to a time-invariant mass transfer flux F_s, it is readily deducible from the appropriate solution to the diffusion equation (equation 4.55 of [10]) that

$$C_0 - C_s = \frac{F_s\delta}{D}\left\{\frac{Dt}{\delta^2} + \frac{1}{3} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\,e^{-Dn^2\pi^2t/\delta^2}\cos n\pi\right\}. \quad (3)$$

Hence

$$F_st = \delta\left\{(C_0 - C_s) - \frac{F_s\delta}{D}\left[\frac{1}{3} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\times e^{-Dn^2\pi^2t/\delta^2}.\cos n\pi\right]\right\}. \quad (4)$$

Equation (4) represents a mass balance for a portion of the sheet of unit area, from which F_st is the quantity of material removed in time t. Where there is no change of thickness δ during transfer, the quantity within the braces can therefore be regarded as a change in thickness averaged concentration for the sheet. The average concentration itself, C_m, is then evidently given by

$$C_m = C_s + \frac{F_s\delta}{D}\left[\frac{1}{3} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} \times e^{-Dn^2\pi^2t/\delta^2} . \cos n\pi\right]. \tag{5}$$

Now for the polymer coatings of present interest, δ changes as transfer proceeds. However if the thickness change δ' occurs over a relatively long time t' such that $\sqrt{Dt'} \gg \delta'$, it is reasonable to suppose that the concentration distribution within the coating of instantaneous thickness δ is the same as that within a sheet of constant thickness δ subject to the same surface flux F_s for the same time. Then equation (5) gives a good approximation to the thickness-averaged concentration within the shrinking coating at any time t in terms of the instantaneous value of δ, provided that the shrinking rate is slow enough to satisfy the condition $t' \gg \delta'^2/D$. Since the relation between coating volume and composition has been shown in Section A to be linear, we can deduce that, for these coatings of non-uniform composition:

$$\frac{\delta'}{\delta_1} = \frac{\phi_{1m} - \phi_{2m}}{1 - \phi_{2m}} \tag{6}$$

where ϕ_{1m} and ϕ_{2m} are respectively the initial and final thickness-averaged volume fractions of swelling agent in the polymer at the beginning and end of the constant rate period, given by C_{1m}/ρ and C_{2m}/ρ (assuming no change of ρ, the coating density, according to Section A).

On these assumptions, using equation (6), we can express the mass-balance over unit area of the shrinking film for the 'constant-rate' period t' as follows:

$$F_st' = \rho\delta' = \rho\delta_1\frac{\phi_{1m} - \phi_{2m}}{1 - \phi_{2m}}. \tag{7}$$

A newly-swollen coating can be taken to have uniform composition throughout; so $\phi_{1m} = \phi_{1s}$, the volume fraction of swelling agent in the polymer phase at its surface, over which the equilibrium vapour pressure is p_s.

For ϕ_{2m}, on the other hand, $= C_{2m}/\rho$, equation (5) gives

$$\phi_{2m} = \phi_{2s} + \frac{1}{3}\frac{F_s\delta_2}{\rho D}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} \times e^{-Dn^2\pi^2t'/\delta_2^2} . \cos n\pi\right] \tag{8}$$

where ϕ_{2s} is the volume fraction in the surface of the polymer at the end of the 'constant rate' period, in equilibrium with vapour at a partial pressure 0·95 p_s.

Now,

$$t' = \frac{\rho\delta'}{F_s} \tag{9}$$

so the exponent of e on the R.H.S. of equation (8) can be written:

$$-\frac{Dn^2\pi^2\rho\delta'}{F_s\delta_2^2} \quad \text{or} \quad -n^2\pi^2\frac{\rho D}{F_s\delta_1} \times \frac{1}{(1 - \delta'/\delta_1)(\delta_1/\delta' - 1)}$$

since $\delta_2 = \delta_1 - \delta'$.
Putting

$$\frac{F_s\delta_1}{\rho D}\left(1 - \frac{\delta'}{\delta_1}\right)\left(\frac{\delta_1}{\delta'} - 1\right) \equiv f_2\left(\frac{F_s\delta_1}{\rho D}, \frac{\delta'}{\delta_1}\right) \tag{10}$$

and

$$f_3\left(\frac{F_s\delta_1}{\rho D}, \frac{\delta'}{\delta_1}\right) \equiv \frac{1}{3}f_2\left(1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} \times e^{-n^2\pi^2/f_2} . \cos n\pi\right) \tag{11}$$

we obtain from equation (8)

$$\phi_{1m} - \phi_{2m} = (\phi_1 - \phi_2)_s - \frac{\delta'}{\delta_2}f_3 = f_1 - \frac{\delta'}{\delta_2}f_3 = f_1 - \frac{f_3}{[(\delta_1/\delta') - 1]} \tag{12}$$

where f_1 is the function of ϕ_1 and χ plotted in Fig. 3. From equations (7), (8) and (12) we have

$$\frac{\delta'}{\delta} = \frac{[(\delta_1/\delta') - 1]f_1 - f_3}{[(\delta_1/\delta') - 1]\{(1 - \phi_1) + f_1\} - f_3} \tag{13}$$

which reduces to

$$f_3 = [(\delta_1/\delta') - 1]f_1 - (1 - \phi_1)$$

or

$$f_3\left(\frac{F_s\delta_1}{\rho D}, \frac{\delta'}{\delta_1}\right) = f_4\left(\frac{\delta'}{\delta_1}, f_1\right) - (1 - \phi_1) \tag{14}$$

where

$$f_4 \equiv \left[\left(\frac{\delta_1}{\delta'}\right) - 1\right]f_1.$$

Equation (14) can be solved to give δ'/δ_1, the maximum allowable fractional shrinkage for a coating of given properties, initial composition and thickness subject to a known mass transfer flux $F_s (= Kp_sM/RT$ for evaporation into a stream of pure air) with the aid of the charts given in Figs. 4(a) and (b). These charts each comprise computed curves of f_3 plotted against δ'/δ_1 with $F_s\delta_1/\rho D$ as parameter, and curves of $f_4 - 0{\cdot}5$, corresponding to a standard or reference value of $\phi_1 = 0{\cdot}5$, also plotted against δ'/δ_1 as abscissa, with f_1 as parameter. The group $F_s\delta_1/\rho D$ having been evaluated, and the value of f_1 having been found from Fig. 3 from knowledge of ϕ_1 and χ, the required value of δ'/δ_1 corresponds to the intersection of the appropriate curves of Fig. 4 if ϕ_1 for the swollen coating has the reference value 0·5. If, on the other hand, ϕ_1 has some other value, inspection of equation (14) shows that the correct point of intersection with the curve of f_3 is that obtained by translating the curve of $f_4 - 0{\cdot}5$ through a distance $\phi_1 - 0{\cdot}5$ along the ordinate. The functional equivalent of this operation is readily performed with the aid of a cursor or subsidiary movable scale, graduated in units of $\phi_1 - 0{\cdot}5$ to the same scale as the ordinate. The cursor is moved along the appropriate curve of $f_4 - 0{\cdot}5$ with its zero graduation on that curve and its edge parallel to the ordinate, until the appropriate ϕ_1 graduation falls on the designated curve of f_3.

When δ' has been thus obtained, t', the duration of the constant rate period, can be found from equation (9).

The condition

$$t' = \frac{\rho\delta' RT}{kp_sM} \gg \frac{\delta'^2}{D} \tag{15}$$

on which the above analysis rests is generally fulfilled *a fortiori* in experiments with laboratory-scale apparatus, because δ' must be kept small to avoid alterations of flow pattern and t' must be made large enough to avoid excessive start-up and shut-down errors. δ', for instance, can conveniently be of the order 10^{-3} cm for reasonable precision of measurement by air gauging, as used in the present experiments, or by hologram interferometry [11]; and for many swollen rubber systems D is of the order $10^{-7} - 10^{-6}$ cm²/s. As the duration of an experiment must certainly be arranged (by choice of swelling agent with sufficiently low p_0) to exceed 100 s, condition (15) will be satisfied in practical cases.

It is apparent from Figs. 3 and 4 that as δ' can be as small as 10^{-3} cm without significant restriction of accuracy of measurement, δ_1, the initial thickness of the swollen coating, may be made as small as 6–7×10^{-3} cm if the system has suitable values of χ and ϕ_1. The use of such thin coatings is advantageous where lateral diffusion within the coating is likely to limit the spatial resolution of local mass transfer determinations, as explained in Section D below; and thin coatings are in any case particularly convenient to apply, using such techniques as latex dipping, knife casting or spraying. In many practical cases, therefore, in which D is in the region 10^{-6}–10^{-7} cm²/s and a low vapour pressure swelling agent is used so that t' is of the order 10^3 s or more, the coating may be considered thin, in the sense that

$$\frac{\delta_1}{\sqrt{Dt'}} < 1. \tag{16}$$

Figure 4(b) is an enlargement of that region of Chart 4(a) appropriate to this common practical case of thin coatings.

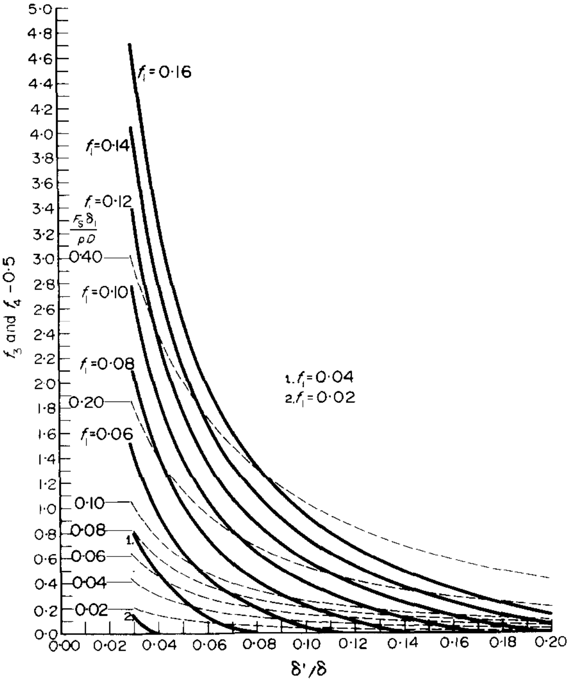

FIG. 4(a). Chart for the determination of the maximum allowable fractional recession, δ'/δ_1, of a swollen coating characterized by f_1 and subject to a constant transfer flux F_s. (Drawn for $\phi_1 = 0{\cdot}5$; for correction for other ϕ_1 values, see text.)

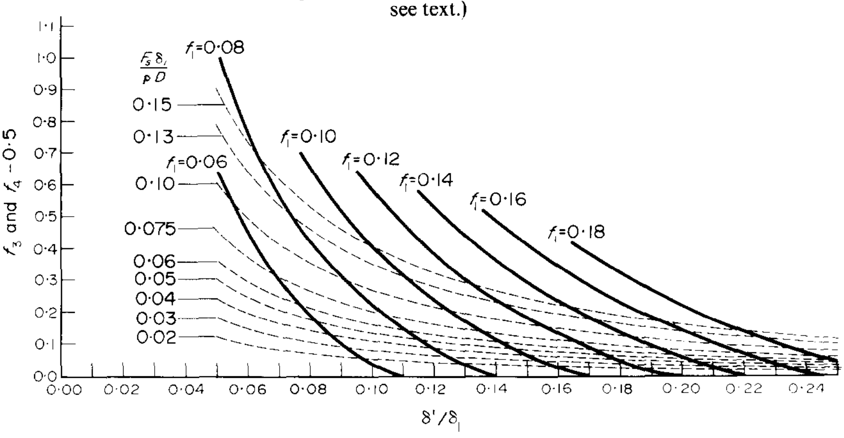

FIG. 4(b). Enlarged portion of Fig. 4(a) for small values of $F_s\delta_1/\rho D$.

It is noteworthy that when the inequality (16) is satisfied the exponential series terms of f_3 become very small compared with unity. From equation (11), f_3 is then given approximately by

$$f_3 = \frac{1}{3}\frac{F_s\delta_1}{\rho D}\left(1-\frac{\delta'}{\delta_1}\right)\left(\frac{\delta_1}{\delta'}-1\right). \qquad (17)$$

Substitution of equation (17) into (13) leads to the equation

$$\frac{\delta'}{\delta_1} = 1 - \frac{f_1 + (1-\phi_1) \pm \sqrt{[\{(f_1+(1-\phi_1)\}^2 - \frac{4}{3}(F_s\delta_1/\rho D)(1-\phi_1)]}}{\frac{2}{3}(F_s\delta_1/\rho D)}. \qquad (18)$$

Equation (18) provides a means, alternative to the use of the chart of Fig. 4(b), of finding δ'/δ_1 for thin coatings satisfying the condition (16) when the mass transfer flux, coating properties and initial conditions are known.

We now compare the observed 'constant-rate' behaviour of the natural latex/methyl salicylate system with that predicted by the above analysis.

Experimental plots of weight loss vs. time for a natural latex coating, initially swollen to different degrees with methyl salicylate and exposed to air streams at each of two different Reynolds numbers in the apparatus of Fig. 2, are shown in Fig. 5. The curves for a given constant air flow rate and different initial proportions of swelling agent are evidently of the same slope and are thus superimposable when a suitable common origin is chosen for the time scales. The resultant curves demonstrate clearly that the transfer rate, as measured by the quotient, total mass transferred (proportional as shown in Section A to the total thickness change) divided by the duration of the experiment, is sensibly constant with time over substantial changes of composition and for considerable periods for heavily swollen coatings. The upper curve of Fig. 5, for instance, falls apparently linearly from an initial composition corresponding to $\phi = 0{\cdot}575$ until about 35 per cent of the original weight of ester has been removed. The densities of the components of this swollen latex system are nearly equal; as their volumes are additive, as shown in Section A, we obtain from these results

$$\frac{\delta'}{\delta_1} = 0{\cdot}20.$$

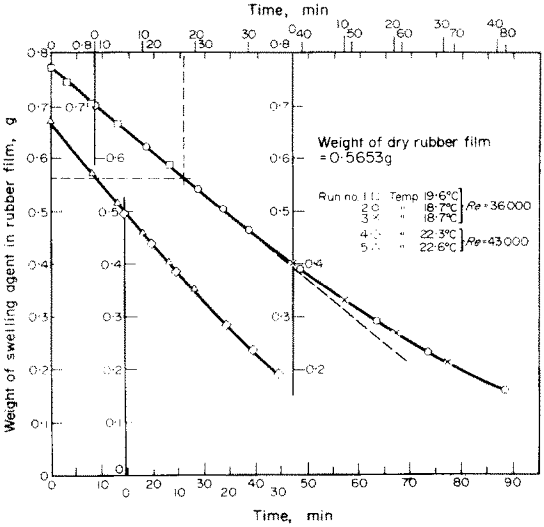

FIG. 5. Time variation of weight of swelling agent in a coating specimen initially swollen to various degrees and exposed to a current of air at (a) $Re = 36000$, (b) $Re = 43000$.

At the rate of transfer obtaining in this experiment, the upper curve of Fig. 5 shows that the corresponding duration of the constant rate period was about 35 min.

δ_1 for the swollen coating was 0·038 cm. From our own measurements of the rate of uptake of methyl salicylate by latex coatings, D, the diffusivity of methyl salicylate in the rubber, is approximately 10^{-6} cm^2/s. We then have

$$\frac{Dt'}{\delta_1^2} = 1{\cdot}45.$$

Also, since $\delta' < \delta_1$, $\delta' < \sqrt{Dt'}$. Hence the coating can be considered thin and its recession slow. The range of its 'constant rate' behaviour should therefore agree with that given by Fig. 4 and equation (18).

To make this comparison, we require an experimental value of χ. The most highly swollen coating used here, having $\phi_1 = 0{\cdot}575$, was near equilibrium with the swelling agent. Equation (1) then gives $\chi = 0{\cdot}72$. For a coating having these values of χ and ϕ_1, Fig. 3 gives $f_1(\phi_1, \chi) = 0{\cdot}16$. Using the F_s value computed from the slope of the upper curve of Fig. 5, together with the value $\rho = 1{\cdot}17$ g/cm^3 from the experiments reported in Section A and the values of ϕ_1, f_1, δ_1 and D given above, equation (18) or Fig. 4(b) gives:

$$\frac{\delta'}{\delta_1} = 0{\cdot}23.$$

Equation (9) gives: $t' = 40$ min.

These calculated values for δ'/δ_1 and t' are in reasonable agreement with those obtained from the experimental data of Fig. 5, viz. 0·20 and 35 min respectively, in view of the fact that there is considerable uncertainty in estimating the point beyond which the slope of the experimental curve is significantly different from its initial value. Moreover, the χ value used in the calculations is to a slight, but unknown, extent too large, as the largest observed ϕ_1 was somewhat below the true equilibrium value.

It is, however, noteworthy that the definition of the 'constant rate' period used here leads to pessimistic estimates of the permissible duration of an experiment. Though a 5 per cent change of instantaneous rate develops after a time interval t', the *integrated* effect of this change on the time-averaged transfer rate determined from the quotient (total weight loss over total time) would remain below the 5 per cent level for a much longer period.

C. *Location of the controlling resistance to mass transfer*

As indicated in the last Section, the rate of transfer from a swollen polymer coating to a stream of fluid will remain close to the initial value only so long as the surface composition of the coating is not greatly different from the original, bulk, composition; that is, so long as there is no significant resistance to transfer within the coating itself. As a corollary, it follows that during the 'constant rate' period the controlling resistance to mass transfer is necessarily in the fluid stream, not in the coating. The above experimental demonstration that a practical coating system shows constant rate behaviour thus provides evidence that the controlling resistance to mass transfer is on the fluid side in these circumstances.

For the conditions of the turbulent air-flow experiments discussed in the last Section, the air-side mass transfer coefficient would be expected to be proportional to $Re^{0 \cdot 8}$. The Reynolds numbers in the experiments of Fig. 5 were 43 000 and 36 000. Their ratio to the power 0·8 is 1·15, in close agreement with the value 1·13 obtained for the temperature-corrected ratio of the slopes of the straight lines of Fig. 5 expressing the measured mass transfer rates, confirming that the controlling resistance is indeed on the air-side.

The apparatus available for these experiments did not allow large airflow Reynolds numbers to be attained, so the above comparison could not be pursued over a great range of conditions. However the comparison between the spatial variation of local air-side mass transfer coefficient and of local shrinkage rate for a cylinder in cross-flow, reported below, confirms the parallelism between these quantities and establishes the controlling influence of the air-side coefficient over a wider range of transfer rates.

D. *Independence of local coating-thickness changes at adjacent sites*

It is evident that condition D would not be fulfilled if the transfer rate over the surface varied sufficiently abruptly from point to point. In that case, a coating which was uniformly impregnated initially could become so unequally depleted and shrunk as transfer proceeded that the swelling agent would migrate to a significant extent through the polymer layer under the influence of the developing lateral concentration gradients. Furthermore, the stress gradients at any point in the coating arising from the non-uniformity of local strain might affect the local shrinkage. For both these reasons the pattern of shrinkage over the coating would not exactly reproduce that of the transfer rate variation.

The following analysis shows that, in practical cases, it can be arranged that lateral migration of the swelling agent has no significant "blurring" effect on the profilometric record of local transfer rate variation over the coating.

In Fig. 6, an element of the swollen coating is bounded by imaginary parallel planes perpendicular to the coating-substrate interface, distance dx apart; for simplicity, the coating

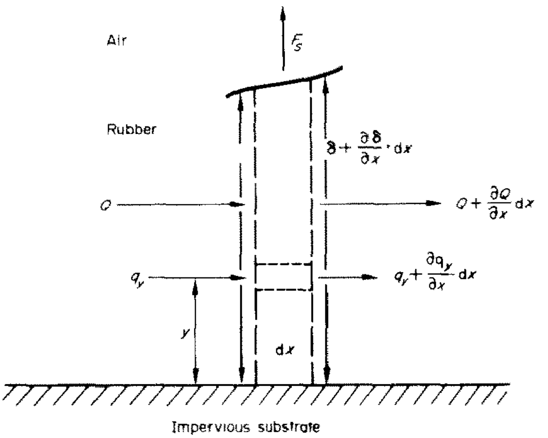

FIG. 6. Nomenclature for lateral and normal (surface) mass fluxes in a swollen surface coating.

thickness is assumed to vary in the plane of the figure only. Q is the lateral flux of swelling agent averaged over the local thickness δ of the coating at one of the imaginary boundaries of this element, and F_s is the local normal flux from the coating-air interface. A mass-balance over the element of width dx and unit depth perpendicular to the plane of the figure gives

$$\frac{\mathrm{d}m}{\mathrm{d}t} \cdot \mathrm{d}x = Q\delta - \left(Q + \frac{\partial Q}{\partial x}\mathrm{d}x\right)\left(\delta + \frac{\partial \delta}{\partial x}\mathrm{d}x\right) - F_s \mathrm{d}x$$

where m is the mass of swelling agent per unit superficial area of the coating.

Hence

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\delta\frac{\partial Q}{\partial x} - Q\frac{\partial \delta}{\partial x} - F_s. \qquad (19)$$

Now

$$Q \equiv \frac{1}{\delta}\int_0^\delta q_y \,\mathrm{d}y = \frac{1}{\delta}\int_0^\delta - D\frac{\partial C}{\partial x}\mathrm{d}y.$$

In the absence of information about the dependence of D on concentration D is assumed constant. We then have

$$Q = -D\frac{\partial}{\partial x} \cdot \frac{1}{\delta}\int_0^\delta C\,\mathrm{d}y = -D\frac{\partial C_m}{\partial x}$$

and

$$\frac{\partial Q}{\partial x} = -D\frac{\delta^2 C_m}{\partial x^2}.$$

Hence

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\delta D\frac{\partial^2 C_m}{\partial x^2} + D\frac{\partial C_m}{\partial x} \cdot \frac{\partial \delta}{\partial x} - F_s. \qquad (20)$$

We have now to determine in what circumstances the first two terms on the right of (20) are negligible compared with the third.

We reduce the problem to a one-dimensional one by the following device. Instead of considering the coating as continuous, in which case the concentration field in the xy plane is essentially two-dimensional, we divide it by imaginary impermeable barriers or yz planes perpendicular to its surface into a number of regions over each of which the normal surface flux is uniform, and within which the concentration field is consequently one-dimensional. Having made the appropriate computations of concentration distribution, we then examine the effect of removing the barriers.

Taking each such isolated region of coating as a plane sheet of uniform thickness δ, having one face impermeable and a time-invariant mass-flux F_s over the other face, we have from equation (7)

$$F_s t = \delta_1 \frac{C_0 - C_m}{1 - (C_m/\rho)} = \delta_1 \rho \frac{C_0 - C_m}{\rho - C_m}. \qquad (21)$$

Hence,

$$F_s > \frac{\delta_1}{t}(C_0 - C_m).$$

If, therefore, after the elapse of some time $t(\leqslant t')$ during which the impermeable barriers are maintained

$$C_0 - C_m \gg \frac{Dt}{\delta_1} \cdot \frac{\partial C_m}{\partial x} \cdot \frac{\partial \delta}{\partial x} \qquad (22)$$

and

$$C_0 - C_m \gg Dt \cdot \frac{\partial^2 C_m}{\partial x^2} \tag{23}$$

then F_s is large compared with the third and second terms respectively on the right-side of equation (20). The lateral diffusion which occurs when the barriers are removed would then have a negligible effect in modifying local rates of recession of the coating during a (short) subsequent period of transfer.

Putting $C_0 - C_m \equiv \Delta C_m$, the change in the thickness-averaged concentration of the coating corresponding to the reduction of thickness $\Delta\delta$, we have from (21)

$$\Delta C_m = (\rho - C_m)\frac{F_s t}{\rho\delta_1} \simeq \rho\frac{\Delta\delta}{\delta_1}.$$

Since $\partial(\Delta C_m) = -\partial C_m$ and $\partial(\Delta\delta) = -\partial\delta$, the conditions (22) and (23) become respectively:

$$\frac{\Delta\delta}{\delta_1} \gg \frac{Dt}{\delta_1^2}\cdot\left(\frac{\partial\delta}{\partial x}\right)^2 \tag{24}$$

and

$$\frac{\Delta\delta}{\delta_1^2} \gg \frac{Dt}{\delta_1^2}\cdot\frac{\partial^2\delta}{\partial x^2}. \tag{25}$$

It is explained in Section B above that practical circumstances often allow Dt'/δ_1^2 to be made of the order unity. This group rarely has a very much smaller value, however; and generally, of course $\Delta\delta/\delta_1 \ll 1$. Conditions (24) and (25) are thus observed throughout the 'constant rate' period in most cases only if the peaks and hollows developed in the coating surface by mass transfer are of 'wave length' substantially greater than the coating thickness. In other words, the coating thickness must be made less than the scale of spatial resolution desired. In practice, the resolution is generally ultimately limited by the fineness of the gauging means.

The mechanical influence of adjacent differently shrunk regions of coating upon one another depends upon the shear modulus of the coating material. As this is not known for the rubbers used in their swollen state, the importance of these lateral mechanical effects cannot be calculated. Their influence on the configuration of the surface of films of swollen natural rubber latex is evidently small, however, when the fractional changes of coating thickness are small. This is shown by the following experiments.

Cylinders coated with swollen latex were placed in a transverse turbulent stream of air. These showed an azimuthal variation of recession substantially identical to the known pattern of local transfer coefficient variation as determined in experiments uncomplicated by lateral diffusion or stress effects. Figure 7 shows (normalized) the measured azimuthal variation of surface recession for rubber-coated and naphthalene-coated 1·3 cm diameter cylinders placed in cross flows of air of the same speed ($Re = 6500$ based on cylinder diameter) and subsequently measured with the same free-jet air gauge having a nozzle 0·5 mm dia. The comparative results are not entirely satisfactory, because although the reproducibility of the

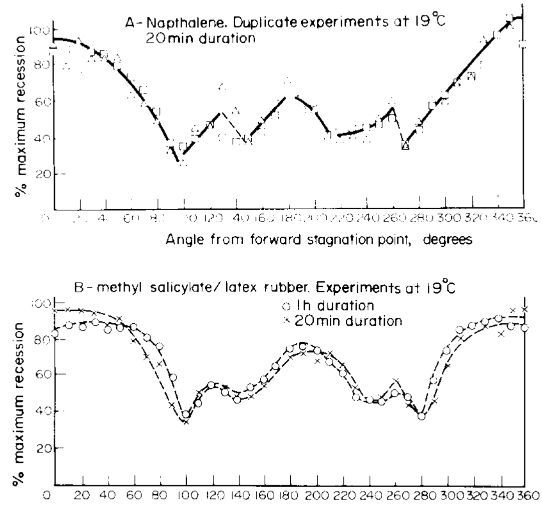

FIG. 7. Normalized azimuthal variation of surface recession for single 1·3 cm. dia. circular cylinders coated (a) with naphthalene, (b) with swollen rubber, placed in hydrodynamically similar cross flows if air ($Re = 6500$).

measurements for the rubber coated cylinder is good, that for the naphthalene coated cylinder is poor, for reasons which were not apparent. But it is evident that there is no systematic difference between the recession profiles for the naphthalene and rubber-coated cylinders. In particular, there is no evidence of additional loss of definition, or spatial resolution, for the latter in regions where the transfer coefficient changes abruptly. It is reasonable to conclude that, in this system, lateral effects within the coating (which was a few tenths of a millimetre thick) do not limit the spatial resolution attainable with a 0·5 mm dia. measuring probe.

E. *Effects of non-uniform coating thickness*

Unless the coating is initially applied as a veneer of callendered sheet, its thickness is likely to vary from place to place over the surface of the model. Dip-coating, for instance, gives surface layers which are satisfactorily smooth externally but whose thickness is made non-uniform by drainage and surface tension effects.

If such inequalities of thickness are not to influence initial rates of transfer, it is evidently simply necessary to use a coating of insoluble polymer all parts of which are swollen to the same composition. This situation obtains with coatings swollen to, or approaching, equilibrium with pure swelling agent or a solution containing it.

From the analysis given in the previous sections it can be seen that variations in coating thickness otherwise present no difficulties or special sources of error in the interpretation of shrinking-rate measurements.* Within a maximum allowable recession and 'constant rate' period computed for the least favourable part of the coating and the maximum mass transfer rate encountered, the coating will give 'constant rate' shrinkage over its entire surface. Because of the additivity of volumes of polymer and swelling agent, local surface recessions of smaller magnitude than the limiting value are direct measures of transfer rate, irrespective of initial coating thickness.

To test these conclusions experimentally, the central rod of the apparatus shown in Fig. 2 was on two occasions coated with films of graded thickness, varying in one case from 2 to $3{\cdot}5 \times 10^{-2}$ cm and in the other from 1·1 to $2{\cdot}2 \times 10^{-2}$ cm thick in the unswollen state. In neither case did the local rate of coating shrinkage during the 'constant rate' period show any significant variation with local coating thickness.

THE DETERMINATION OF ABSOLUTE VALUES OF TRANSFER COEFFICIENTS

The above results establish that the local rates of shrinkage over a coated mass transfer model are, under proper experimental conditions, proportional to the corresponding local convective mass transfer coefficients. To obtain absolute values of these coefficients from shrinkage rate measurements, one must know:

(i) The density of the shrinking phase, and

(ii) The concentration driving force, or vapour pressure over its surface.

To generalize the results in dimensionless form and, in particular, to use them for predicting heat transfer coefficients, it is further necessary to know:

(iii) The diffusivity of the vapour of the swelling agent in the experimental fluid.

(i) For the latex rubber/methyl salicylate coatings used here, the density was found from the results reported in Section A above to have the value 1·17 g/cm^3.

The determination of the quantities (ii) and (iii) for this system will now be described.

(ii) *Vapour pressure measurements.* Measurements of the vapour pressure of methyl salicylate over heavily swollen ($0{\cdot}5 < \phi < 0{\cdot}57$) latex coatings at various temperatures were obtained by a transpiration method in the apparatus shown in Fig. 8. The vapour

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* Gross irregularities of coating thickness due to substantial differences of figure between coating and substrate surfaces can, however, introduce a considerable practical difficulty. The flat outer surface of a coating knife-cast on an uneven substrate, for instance, does not retain its original smooth character when swollen to equilibrium, but tends then to reproduce the conformation of its under- or substrate-side.

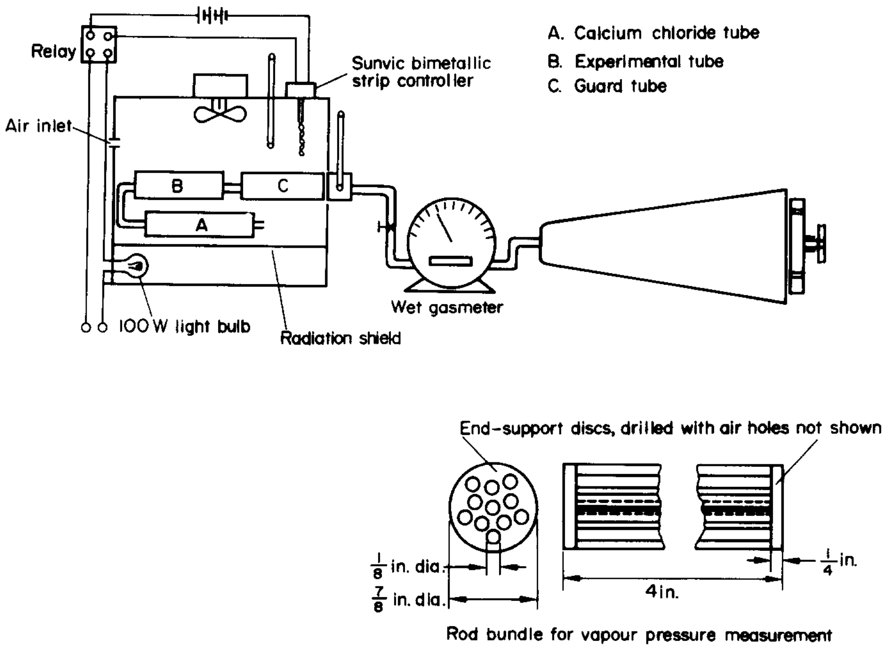

FIG. 8. Apparatus for vapour pressure measurement over swollen coatings by the transpiration method.

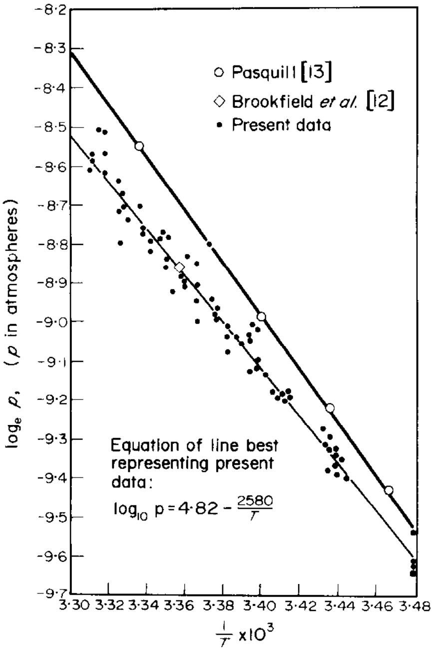

FIG. 9. Vapour pressure of methyl salicylate over natural rubber swollen to approximately twice its dry volume, as a function of temperature.

pressure values are plotted as a function of temperature in Fig. 9.

A cluster of long slender rods or wires coated with polymer swollen nearly to equilibrium was exposed to a slow metered flow of dry air in a temperature controlled environment. The vapour pressure was calculated from the measured loss in weight of the coated rod cluster, on the assumption that the exit air was in equilibrium with the swollen coating. This supposition was checked by varying the air flow rate and by periodic weighings of a guard tube placed downstream of the main apparatus, containing a swollen rubber film supported on wire-gauze.

The majority of the experimental points lie within 4 per cent of a linear plot of log p vs. $1/T$, though several points are much more widely scattered. No correlation was found between swelling agent concentration and degree of deviation from the line within the range of coating composition examined.

According to the Flory–Huggins equation, the vapour pressure over a polymer swollen with at least its own dry volume of ester, as in the present experiments, should be about 1 per cent or less below that of the pure ester at the same temperature, for a system in which $\chi = 0{\cdot}72$ as deduced in the present case from the evidence of Section B. Our data agree with the value at 25°C quoted for the pure ester by Brookfield *et al.* [12], but fall 9–20 per cent below the results of Pasquill [13] and Ramsay and Young [14]. A 9–20 per cent difference between the vapour pressure of the swollen coating and the pure ester would signify a value of χ less than $\frac{1}{2}$; such a low value of χ would be inconsistent with the apparent insolubility of latex rubber in methyl salicylate. One must conclude that the present data accord with the only value given by Brookfield in the temperature range of interest, but are at some temperatures significantly below values predicted when Pasquill's measurements are substituted in the Flory–Huggins equation.

(iii) *Diffusivity measurements.* For laminar flow in an annular channel, the mass transfer coefficient at a point a known distance downstream of the commencement of the transferring section is expressible from first principles in terms of the diffusivity, stream properties and apparatus dimensions. In turbulent flow, the mass transfer coefficient at a point far downstream of the commencement of the transferring section can be estimated from well established empirical correlations, again involving the diffusivity. Measurements of both laminar and turbulent flow transfer coefficients were used in the present work to obtain diffusivity values.

In the laminar flow apparatus, the coated cylinder forming the transferring section of the inner wall of the annular channel was 3·2 cm dia., the internal diameter of the outer (non transferring) tube being 4·7 cm. The non-transferring upstream section of the annular channel, uniform with the test section and smoothly jointed to it, was over twenty hydraulic diameters long, ensuring that the fluid stream entering the transferring section had a fully developed laminar flow profile. The apparatus used in the experiments with turbulent flows was that shown in Fig. 2.

In the turbulent flow experiments, calculation showed that the ester concentration in the issuing air was always very small compared with the equilibrium concentration. In the laminar flow system, however, this was not so and allowance had here to be made for the streamwise variation of concentration driving force when calculating mass transfer coefficients from recession measurements. In the scheme of computation used for the laminar flow results, the length of the annulus was divided into 1·25 cm sections and the bulk concentration of salicylate in the air in each section was taken as the sum of the contributions from all sections upstream.

Laminar-flow mass transfer coefficients thus computed from coating-thickness measurements at various locations were plotted against distance from the commencement of the transferring section for each of the four Reynolds numbers used. Forty transfer coefficient values interpolated from the four smoothed plots were then used in plotting the upper line of Fig. 10, whose slope gives the Schmidt number of the methyl salicylate/air system.

Figure 10 was constructed in the following way. The lower curve is a plot of theoretical values of $\bar{x}\,.\,Sh$ vs. $\bar{x}$ for laminar flow in an annular channel of the radius ratio used here. This curve is based directly on numerical values of Nu and $\bar{x}'$ computed by Lundberg *et al.* [15] from a Graetz-type treatment of the corresponding thermal problem (their 'Solution of the Third Kind', with a step change in the inner wall temperature), interpolated for the required value of the radius ratio. As the quantity $\bar{x}\,.\,Sh \equiv kx_1/\nu\,.\,Re$, plotted along the left-hand axis of Fig. 10, does not involve the diffusivity of the salicylate/air system, values of $\bar{x}$ corresponding to experimental values of k at known x_1 and Re can be read from this curve on the horizontal axis. These $\bar{x}$ values are plotted against corresponding values of the group $x_1/d\,.\,Re$, which

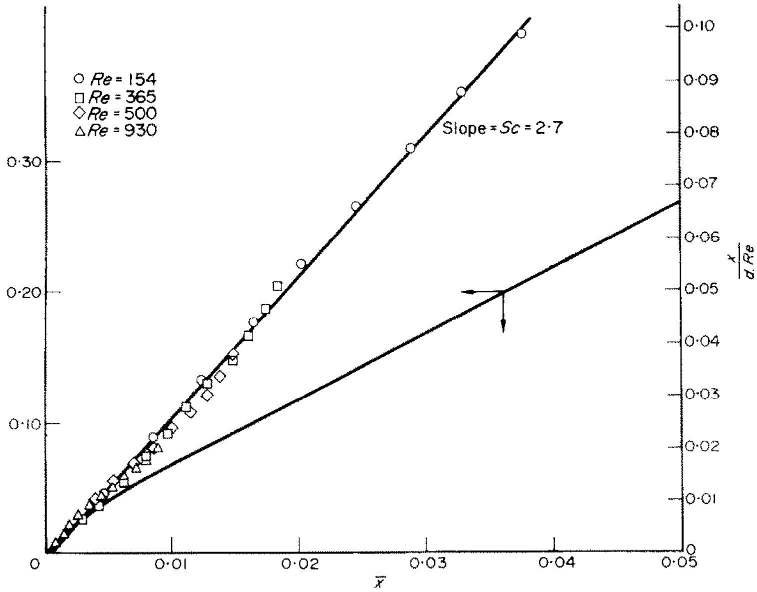

FIG. 10. Graphical construction for the computation of Schmidt no. for the methyl salicylate/air system from experimental measurements of mass transfer coefficients for fully developed laminar flow near the entrance to the transferring section of an annulus.

are represented on the right-hand axis, to give the upper line, of slope $x_1/d\,.\,Re/\bar{x} \equiv Sc$.

All forty points plotted in this way lie within 10 per cent of the best straight line drawn through them; the data points for the lowest Reynolds number used (154), covering the largest range of variables plotted, show a scatter of only ±3 per cent about this line. The slope of the plot, $Sc = 2{\cdot}7$, corresponds to $D_g = 0{\cdot}055$ cm²/s for the methyl salicylate/air system at 20°C.

Figure 11 shows the excellent agreement between the smoothed curve representing the experimentally determined streamwise variation of mass transfer coefficient at $Re = 154$ with theoretical values interpolated from the calculations of Lundberg *et al.* for the present radius ratio. This agreement provides further evidence of the soundness and potentialities of the experimental technique. The best fit with theory for this particular set of data corresponds to a D_g value of 0·057 cm²/s rather than the 0·055 cm²/s which represents the mean of all the data.

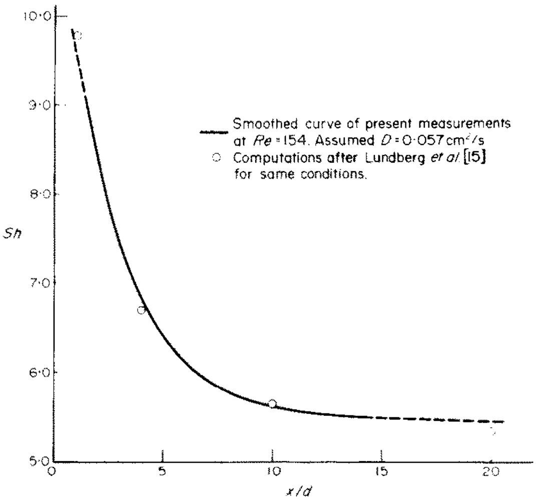

FIG. 11. Streamwise variation of laminar flow mass transfer coefficient in an annulus of radius ratio 0·68 at an airflow $Re = 154$. Comparison of results obtained by the shrinking-coating method with theory, assuming $Sc = 2{\cdot}6$ (i.e. $D_g = 0{\cdot}057$ cm²/s).

The turbulent-flow far-downstream mass transfer data also give the value $D_g = 0{\cdot}055$ cm²/s as the mean of eleven determinations at temperatures between 19 and 23°C in the airflow Reynolds number range 34000–43000. The maximum deviation of individual values from this mean was 10 per cent. The calculations were based on the empirical correlation of Wiegand [16], which in terms of mass transfer becomes:

$$\frac{kd}{D_g} = 0{\cdot}023\, Re^{0{\cdot}8}\, Sc^{0{\cdot}4}\, (d_2/d_1)^{0{\cdot}45}.$$

Wiegand's equation is in good agreement with the heat transfer data of McMillen and Larson [17] for similar values of d_2/d_1.

Our concordant experimental values of the diffusivity of methyl salicylate in air at 20°C are in excellent agreement with that estimated from kinetic theory, viz. $D_g = 0{\cdot}056$ cm²/s [18], though much below the values obtained by Brookfield *et al.* [12].

CONCLUSION

We conclude that rubber surface coatings, swollen with suitable volatile substances, can conveniently serve in place of volatile solid coatings in the profilometric determination of air-side local mass transfer coefficients when air-gauging or other non-contacting means is used to measure the surface recession. In accordance with the general theory developed here, the conditions may be so chosen, with the aid of the graphical solution of the appropriate equations presented in Fig. 4, that such coatings maintain shrinkage-rates effectively proportional to air-side transfer coefficients over substantial changes of swollen thickness at convenient rates of mass transfer, and show no observable limitation of spatial resolution in recording local variations of mass flux.

Coagulant dipped latex rubber coatings, in particular, swollen with a suitable ester, display the advantage over volatile solid coatings of not requiring re-deposition for each experiment; they can apparently be reactivated any number of times by re-immersion in ester. As indicated by Figs. 4 and 5, such coatings of 0·01–0·02 cm dry thickness, swollen initially to about $2\frac{1}{3}$ times this thickness with methyl salicylate, maintain a shrinkage rate nearly proportional to the air-side transfer coefficient at moderate rates of transfer over approximately a 20 per cent change of swollen thickness. The use of other esters allows transfer rates to be measured at other (generally higher) Schmidt numbers, over at least a three-fold range, when air is the experimental fluid.

The physical properties of the methyl salicylate/latex rubber system necessary for the absolute determination of mass transfer coefficients and for the estimation of heat transfer coefficients from corresponding mass transfer measurements are as follows, according to our measurements:

Physical properties of unvulcanized natural latex rubber/methyl salicylate coatings at approximately 100% swelling

Coating density at 20°C = 1·17 g/cm³

Methyl salicylate vapour-pressure over coating, p atmospheres at T°K:

$$\log_{10} p = 4{\cdot}82 - \frac{2580^*}{T}$$

Diffusivity of methyl salicylate in air at 20°C = 0·055 cm²/s

Molecular weight of methyl salicylate = 152

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* Our more recent measurements with methyl salicylate give substantially higher vapour pressure values and suggest that the vapour pressure (but not the diffusivity) of apparently pure samples of this ester vary markedly with sample origin or age. When making absolute measurements of mass transfer coefficients using methyl salicylate, therefore, we recommend that the vapour pressure of the batch of ester used be determined at the time of the experiment.

More recently, we have identified suitable esters whose vapour pressures are not subject to this uncertainty. Ethyl salicylate, in particular, shows no such variability among different samples, and our measurements of its properties accord with published data. (See p. D-130 of [14]).

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DETERMINATION EXPERIMENTALE DES COEFFICIENTS DE TRANSFERT MASSIQUE PARIETAL AVEC UTILISATION D'UN REVETEMENT DE LA SURFACE PAR UN POLYMERE

Résumé—On décrit ici une nouvelle technique profilométrique de détermination des coefficients de transfert massique local sur des surfaces solides et on déduit des principes fondamentaux les conditions de son application pratique avantageuse.

Au lieu des revêtements volatils ou solubles généralement utilisés dans un travail profilométrique, les revêtements utilisés dans la méthode décrite ici sont composés d'un polymère non volatil capable d'absorber des agents dilatants volatils ou solubles. Les flux de transfert d'un agent dilatant vers ou depuis une surface par un courant de fluide expérimental peuvent alors être déduits de mesures des taux de dilatation ou de contraction du revêtement. Le système présente l'avantage que le revêtement lui-même ne nécessite pas de renouvellements fréquents; pour chaque expérience il peut être réactivé par la décharge d'un agent dilatant accumulé ou par sa réimpression dans un bain dilatant. Un autre avantage est la facilité d'opérer avec des nombres de Schmidt variables; ceci peut être fait en changeant seulement l'agent dilatant, sans changer le fluide expérimental ni le revêtement de polymère. De plus cette technique offre la possibilité d'étudier différentes situations de transfert pariétal qui ne pourraient être traitées par les méthodes conventionnelles.

Dans une analyse du case où le revêtement est initialement chargé d'agent dilatant, on montre quels sont les systèmes convenables polymère-agent dilatant et comment les conditions opératoires peuvent être choisies de telle façon que les taux locaux de dilatation du revêtement donnent une mesure précise des coefficients locaux de transfert massique à la paroi. Les résultats essentiels sont donnés pour un système pratique de revêtement dont le comportement est conforme à l'analyse.

DIE EXPERIMENTELLE BESTIMMUNG DES STOFFÜBERGANGSKOEFFIZIENTEN VON OBERFLÄCHENÜBERZÜGEN AUS PLASTISCHEN POLYMEREN

Zusammenfassung—Es wird eine neue profilometrische Methode zur Bestimmung der örtlichen Stoffübergangskoeffizienten an festen Oberflächen beschrieben. Die Bedingungen für ihre erfolgreiche und vorteilhafte praktische Anwendung werden von den Grundlagen her abgeleitet.

Anstelle der gewöhnlich in profilometrischen Arbeiten verwendeten flüchtigen oder löslichen Oberflächenüberzüge, bestehen die hier verwendeten Materialien aus nichtflüchtigen Polymeren, die flüchtige oder lösliche Quellstoffe aufnehmen können. Der zeitliche Übergang der Quellkomponente an der Oberfläche von oder zur Versuchsflüssigkeit kann aus Messungen des gequollenen oder geschrumpften Überzugs bestimmt werden. Diese Methode hat den Vorteil, dass der Überzug keiner häufigen Erneuerung bedarf; für jeden neuen Versuch genügt eine Reaktivierung entweder durch Abgabe angesammelter Quellstoffe oder durch deren Aufnahme im Quellbad. Von weiterem Vorteil ist die leichte Veränderlichkeit der Schmidt-Zahl, die allein durch Änderung des Quellstoffes, ohne Veränderung der Versuchsflüssigkeit oder des Polymerüberzuges erreicht wird. Diese Methode gibt auch eine Möglichkeit zur Untersuchung des Stofftransports von Wand zu Wand, die nach konventioneller Technik nicht leicht zu erreichen ist.

In einer allgemeinen Analyse für gequollene Überzüge werden die praktischen Möglichkeiten für die genaue Messung der örtlichen Stoffübergangskoeffizienten aus der örtlichen Überzugsschrumpfung gezeigt. Es werden die wesentlichen Daten für einen Überzug angegeben, der die analytischen Voraussagen wiedergibt.

ЭКСПЕРИМЕНТАЛЬНОЕ ОПРЕДЕЛЕНИЕ КОЕФФИЦИЕНТОВ ПЕРЕНОСА МАССЫ МЕЖДУ СТЕНКОЙ И ЖИДКОСТЬЮ С ПОМОЩЬЮ ПЛАСТИФИЦИРОВАННЫХ ПОЛИМЕРНЫХ ПОКРЫТИЙ ПОВЕРХНОСТИ

Аннотация—Описан новый профилометрический метод определения локальных коэффициентов переноса массы на твердых поверхностях. Исходя из основных принципов, определены условия его успешного практического применения.

Вместо обычно используемых в профилометрических измерениях летучих или растворимых поверхностных покрытий в описываемой здесь методе применяются покрытия, состоящие из нелетучего полимера, способного адсорбировать летучие или растворимые вызывающие набухание вещества. При этом скорость переноса агента набухания потоком жидкости к поверхности или от нее можно вывести по данным измерения скорости набухания или усадки покрытия. Эта система имеет то преимущество, что не требует частого повторного покрытия; для каждого нового опыта покрытие может активироваться за счет освобождения от аккумулированного вызывающего набухание вещества, или погружения поверхности в ванну с этим веществом. Следующим преимуществом является то, что можно легко изменять значения числа Шмидта, изменяя только агент набухания и не изменяя жидкости или полимерного покрытия. Кроме того, этот метод дает возможность исследовать перенос массы от стенки к стенке, с трудом поддающийся исследованию обычными методами.

В общем анализе случая, когда вначале покрытие пропитывается веществом, вызывающим набухание, показано, как практически выбирать соответетвующие системы полимер-агент набухания и рабочие условия, чтобы по локальным скоростям усадки покрытия измерять локальные коэффициенты переноса массы от жидкости. Приведены данные по системе покрытий, используемых на практике, и показано совпадение с теоретическими результатами.