A Drop Dispersal Model for Rinsing

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A new theory for convection-free rinsing of flat plates was developed to include the drop dispersal mechanism as well as the previously considered diffusion mechanism. Cases where carryover is unequal to dragout were also included in the model. Based on film distribution data, the model offers better agreement with rinse data. The effect of drain time on film distribution and bottom drop volume was also investigated.

The removal of a contaminant-containing solution from a solid body by dipping the solid in a tank of water is common practice, but the mixing processes are not well understood. Although the desirability of predicting mixing effectiveness in rinsing has been recognized for some commercial uses (*5*), little theoretical progress has been made. Only simple systems have been studied (*4*).

One parameter developed to describe rinsing effectiveness was the rinse residual U, which was defined as the ratio of the mass of containment adhering after rinsing to that adhering before rinsing. Use of this ratio led to the following design equation (*5*)

$$C_D = U V_c C_c / V_D \tag{1}$$

where C and V are concentrations and volumes respectively. The subscripts c and D respectively refer to the process carryover which arrives at the rinse tank and the dragout which leaves the rinse tank.

One theoretical prediction of the rinse residual has been developed. Called the diffusion model, it was derived for the rinsing of vertical flat plates in which dragout and carryover volumes were identical. In simplified form, the prediction was given by the following function of area A, mass diffusivity D, and contact time t (*6*):

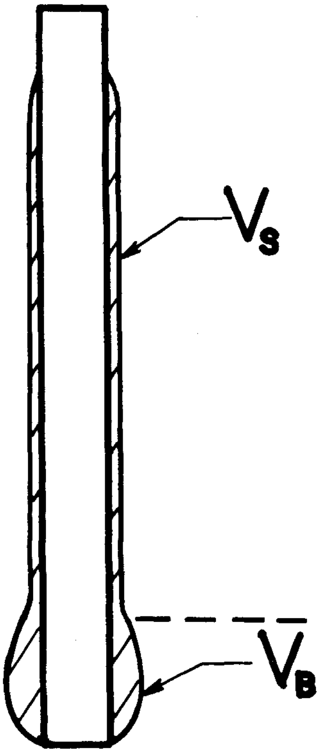

Fig. 1. Film distribution on a flat plate.

$$U = \frac{V_c}{A\sqrt{\pi D t}} \tag{2}$$

Although the square root influence of time and diffusivity predicted by Equation (2) agreed with data, the predicted magnitudes of U were appreciably higher than those found experimentally. Differences of 45 ± 15% were observed and were attributed to secondary modes of mass transfer.

The secondary mechanism for flat plate rinsing of solutions of water-like densities was drop dispersal at entry (*5*). This mechanism described the spread of the bottom drop over the rinse water surface as soon as the drop contacted the rinse water. Consideration of drop dispersal emphasized the importance of the bottom drop. The need for quantitative description of the film distribution in carryover led to a preliminary study of film distribution. Results of the study (*4*) were used to plan the investigation reported below.

The main purposes of this paper are to derive a drop dispersal model for rinsing and to test the theory with data. The paper also presents a new and more accurate method of measuring bottom drop volumes. Volumes measured by the new method were used for testing the drop dispersal model and for film distribution studies.

The work here is limited to flat plate geometries and to negligible convection; the latter implies equal density and viscosity in all liquids (carryover, rinse, and dragout). In addition, conditions are chosen so that top drops and other pools (*4*) are not present in the films and that drippage does not occur.

FILM PARAMETERS

The thickness of the film adhering to a flat plate immediately before entry into a rinse tank is similar to that shown in Figure 1; it is not uniform (*4*). The film thickness at the bottom of the plate was found in photographs (*3*) to be so large that it was characterized separately from the rest of the adhering film. The thick film was called the bottom drop.

Adopting the previous notation (*4*), we take V_B as the bottom drop volume up to some selected boundary. The volume of the side film V_s is defined by difference:

$$V_s \equiv V_c - V_B \tag{3}$$

PART I. THEORY

Statement of the Model

To describe the mass transfer which occurs in rinsing in terms of two mechanisms, diffusion and drop dispersion, the following idealized model is proposed.

After leaving the process tank, the plate is covered with a film of average thickness, $L_c = V_c/A$, having a contaminant concentration C_c. When the plate touches the water, the bottom drop volume V_B is dispersed at the surface; removal of V_B is considered complete. The resultant adhering volume on the plate V_s is considered to be uni-

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formly distributed, with thickness $L_s = V_s/A$. This film is not in fluid motion while it is in the rinse tank or while it is being inserted. See Figure 2.

Diffusion then occurs through the L_s film in the x direction toward the tank wall at a distance L_T.

Upon removal, a new film of uniform thickness $L_D = V_D/A$ and composition C_D adheres rigidly to the solid object without motion. In general L_D is unequal to L_c, and can be either larger or smaller.

The model improves the previously reported diffusion model (shown in Figure 3) in two ways. First, drop dispersal is considered so that the initial film thickness is L_s instead of L_c. Second, dragout is not necessarily equal to carryover ($V_D \neq V_c$).

Derivation of the Theory

The drop-dispersal, diffusion model may be expressed as one-directional unsteady molecular diffusion of one component through another. Mathematically it involves Ficks second law, vanishing gradients at the two walls, and the initial conditions. Except for the values of film thickness, the problem is identical to that solved for the diffusion model; therefore we follow that development (*6*). We write the concentration profile from equation (7) of the previous paper (*6*).

$$C(x, t) = \frac{C_c L_s}{L_T} + \frac{2C_c}{\pi} \sum_{n=1}^{\infty} \frac{\sin(n\pi L_s/L_T)\cos(n\pi x/L_T)}{n \exp(Dn^2\pi^2 t/L_T^2)} \tag{4}$$

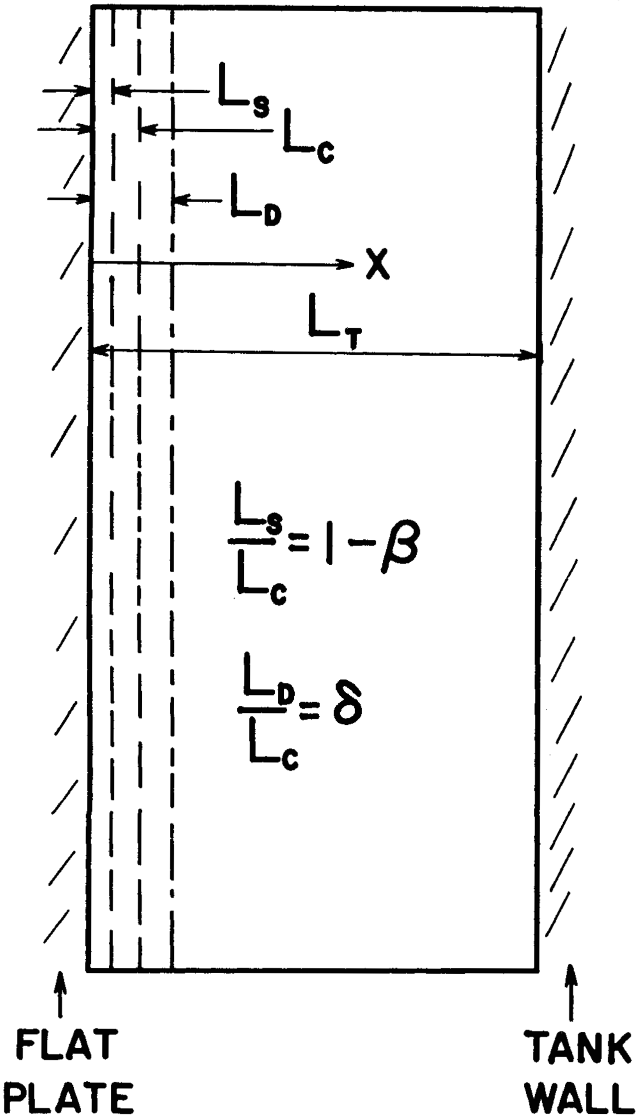

Fig. 2. The drop dispersal model.

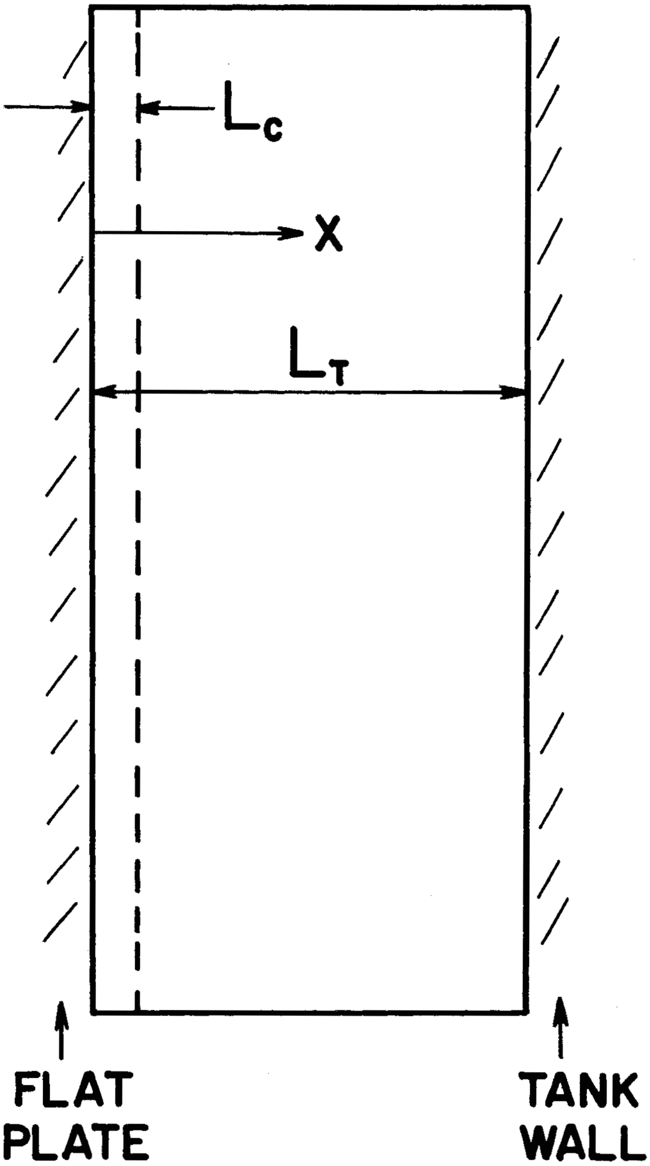

Fig. 3. The diffusion model.

From Equation (1) and evaluation of C_D, we have the U prediction:

$$U = \frac{\int_0^{L_D} C\,dx}{C_c L_c} \tag{5}$$

Substituting Equation (4) into Equation (5), we have

$$U = \frac{L_s L_D}{L_T L_c} + \frac{2}{L_c \pi} \sum_{n=1}^{\infty} \left(\frac{L_T}{n\pi}\right) \frac{\sin(n\pi L_s/L_T)\sin(n\pi L_D/L_T)}{n \exp(Dn^2\pi^2 t/L_T^2)} \tag{6}$$

This series may be replaced for evaluation purposes (*6*) by an integral

$$U = \frac{L_s L_D}{L_T L_c} + \int_0^{\infty} \left(\frac{2L_T}{n^2\pi^2 L_c}\right) \frac{\sin(n\pi L_s/L_T)\sin(n\pi L_D/L_T)}{\exp(Dn^2\pi^2 t/L_T^2)}\,dn \tag{7}$$

To simplify, replace n by u using a change of variable

$$u = n^2\left(\frac{D\pi^2 t}{L_T^2}\right) \quad \text{or} \quad n = \left(\frac{u}{Dt}\right)^{1/2} \frac{L_T}{\pi}$$

Thus Equation (7) becomes

$$U = \frac{L_s L_D}{L_T L_c} + \int_o^\infty \frac{\sqrt{Dt}}{\pi L_c} \sin\left(\frac{uL_s}{Dt}\right)^{1/2} \sin\left(\frac{uL_D}{Dt}\right)^{1/2} e^{-u} u^{-3/2} du \qquad (7a)$$

Expanding each sin term in series, multiplying each series, and replacing with the Gamma function

$$U = \frac{L_s L_D}{L_T L_c} + \sum_{m=1}^{\infty} \frac{\sqrt{Dt}}{\pi L_c} \left(\frac{L_D}{\sqrt{Dt}}\right) \left(\frac{L_s}{\sqrt{Dt}}\right)^{2m-1} D_m \sqrt{\pi} \qquad (7b)$$

where

$$D_m = (-1)^{m-1} \frac{\Gamma\left(m - \frac{1}{2}\right)}{\Gamma\left(\frac{1}{2}\right)} \left[\frac{1}{1!(2m-1)!} + \frac{(L_D/L_s)^3}{3!(2m-3)!} + \frac{(L_D/L_s)^5}{5!(2m-5)!} + \ldots\right] \qquad (8)$$

or

$$U = \frac{L_s L_D}{L_T L_c} + \frac{L_D}{L_c\sqrt{\pi}} \sum_{m=1}^{\infty} D_m \left(\frac{L_s}{\sqrt{Dt}}\right)^{2m-1} \qquad (7c)$$

In terms of volumes, Equation (7*c*) is

$$U = \frac{V_s V_D}{V_T V_c} + \frac{V_D}{V_c\sqrt{\pi}} \sum_{m=1}^{\infty} D_m \left(\frac{V_s}{A\sqrt{Dt}}\right)^{2m-1} \qquad (7d)$$

For the first three terms in the series, Equation (7*d*) is

$$U = \frac{V_s V_D}{V_T V_c} + \frac{V_D}{V_c\sqrt{\pi}} \left\{ \left(\frac{V_s}{A\sqrt{Dt}}\right) - \frac{1}{12}\left(\frac{V_s}{A\sqrt{Dt}}\right)^3 \left[1 + \left(\frac{V_D}{V_s}\right)^2\right] + \frac{1}{160}\left(\frac{V_s}{A\sqrt{Dt}}\right)^5 \left[1 + \frac{10}{3}\left(\frac{V_D}{V_s}\right)^2 + \left(\frac{V_D}{V_s}\right)^4\right] - \ldots \right\} \qquad (9)$$

Equation (9) is the drop dispersal theory in general form.

The One Term Form of the Theory

In most rinsing cases the tank volume is much larger than the side film volume ($V_T >> V_s$) so that the first term in Equation (9) is negligible. Except at very short times when $tDA^2 < V_s^2$, the higher order terms in Equation (9) are also negligible (*6*). Thus Equation (9) can usually be described to three figures by

$$U = \frac{V_D}{V_c\sqrt{\pi}} \left(\frac{V_s}{A\sqrt{Dt}}\right) \qquad (10)$$

In terms of the bottom drop volume, Equation (10) is

$$U = \frac{V_D}{V_c} \frac{(V_c - V_B)}{A\sqrt{\pi Dt}} \qquad (10a)$$

It is convenient to express all volumes relative to carryover V_c. Thus we define the bottom drop fraction β as:

$$\beta \equiv V_B/V_c \qquad (11)$$

It is also convenient to define a dragout fraction

$$\delta \equiv V_D/V_c \qquad (12)$$

In this way, the volumes V_c, V_D, V_B, and V_s may be expressed in terms of one volume V_c and two dimensionless quantities, β and δ. Equation (10*a*) becomes

$$U = \frac{V_c\,\delta(1-\beta)}{A\sqrt{\pi Dt}} \qquad (13)$$

Equation (13) is a convenient form of the drop dispersal theory for verification tests and for design purposes.

Special Cases

The three important special cases of the theory are the unequal dragout model, the bottom drop model, and the diffusion model.

When the bottom drop fraction is neglected ($\beta = 0$), Equation (13) becomes the unequal dragout model

$$U = \frac{V_c\,\delta}{A\sqrt{\pi Dt}} \qquad (14a)$$

or

$$U = \frac{V_D}{A\sqrt{\pi Dt}} \qquad (14)$$

Where dragout and carryover volumes are equal ($\delta = 1$), Equation (13) reduces to the bottom drop model

$$U = \frac{V_c(1-\beta)}{A\sqrt{\pi Dt}} \qquad (15a)$$

or

$$U = \frac{V_c - V_B}{A\sqrt{\pi Dt}} \qquad (15)$$

When the bottom drop fraction is neglected and dragout equals carryover ($\beta = 0$ and $\delta = 1$), Equation (13) reduces to the diffusion model [see Equation (2)].

The unequal dragout model and the bottom drop model, Equations (14) and (15), were first derived as extensions of the diffusion model in two unpublished reports in 1961. The unequal dragout model was developed first. The bottom drop model was later derived by Li in a more general approach which suggested the method for developing the drop-dispersal model, Equation (13). Details of the original development of Equation (14) and the two other methods for deriving Equation (15) are included in thesis form (*3*).

Tests of Special Cases

The diffusion model predicts the effect of time and diffusivity properly but predicts a magnitude of U which is about 45% above experimental values (*6*). Therefore the effect of t and D in Equations (13), (14), and (15) appears to be proper for the conditions considered.

Tests of the unequal dragout model and the effect of δ are discussed in Part II. Tests of the bottom drop model and the effect of β are discussed in Part IV.

PART II. TEST OF THE UNEQUAL DRAGOUT THEORY

The case of $V_c \neq V_D$ and $\beta = 0$ is described by the unequal dragout model, Equation (14) or (14*a*). The derivation of Equation (14) has not been published before but the equation was presented without proof in 1962 (*7*) in order to report the effect of δ when $\delta \neq 1$.

Equation (14*a*) was given an experimental test by using different withdrawal speeds for the process and rinse baths to obtain different carry-over and dragout volumes. Based on measured values of carry-over and dragout volumes and measured values of rinse residual, Equation (14*a*) qualitatively predicted the effect of δ found experimentally (*7*), both for $\delta > 1$ and $\delta < 1$.

Equation (14) indicates an unexpected result. For a constant dragout volume, the model predicts that the rinse residual is not influenced by changes in carry-over volume. The influences of variations in carry-over and bottom drop volumes are present, however, if the higher order terms in Equation (9) are included.

Because unequal dragout conditions often occur in industrial applications, it is suggested that the model be tested more thoroughly, both in terms of precision and range of conditions.

PART III. MEASUREMENT OF THE BOTTOM DROP

Tests of the effects of diffusivity, time, and dragout fraction relevant to the drop dispersal Equation (13) have been reported (*6, 7*). To test the influence of the bottom drop fraction, we have chosen the conditions of Equation (15).

In order to predict rinse residual U by Equation (15), accurate measurements of the bottom drop volume are needed. The second part of this paper is devoted to an experimental study of bottom drop volume, V_B. Precise measurements of V_B are more difficult to obtain than those for V_c and V_D.

Two methods for estimating the volume of the bottom drop adhering to a flat plate have been suggested and tested. Both the Mattson scoop method and the Barbolini touch method are indirect methods involving contact with another liquid. Results differed significantly; for example volumes of 0.13 and 0.41 ml were obtained (at the same conditions) by the scoop and touch method respectively. From consideration of the experimental methods, it was felt that the Barbolini touch method is the more accurate of the two; however, the actual volume probably is somewhat intermediate to the values estimated by the two methods. Quantitative details and results of the touch method and a qualitative description of the scoop method are given elsewhere under the heading *film distribution* (*4*). Further discussion has been given in thesis form (*3*).

To avoid the complex dynamics occurring when liquid films touch a rinse bath surface, it was decided to measure V_B in this work without mixing in other liquids.

The volume of the bottom drop is a transient; V_B changes with the drain time, which is the amount of time which has elapsed after withdrawal. This has been overlooked in some work. For example, the results of Tallmadge and Barbolini (*4*) do not state the drain time used. However, it is estimated that drain time was about 20 sec. in that work, based on the time required to transport the plate horizontally from the contaminant bath to the rinse tank.

Because the bottom drop volume is a transient, it was decided to measure the volume with a method which operated as quickly as possible. A freeze method was selected.

APPARATUS AND ANALYTICAL

The apparatus and analytical procedure were identical to those described earlier (*4, 5*) except as noted in thesis form (*3*) and, in brief, below.

The new, stainless steel flat plate was 14.0 cm. long, 14.6 cm. wide and 0.165 cm. thick. The plate was similar to that used previously by three experimenters except that more care was taken to insure uniform thickness, straight edges, and a better mechanical finish. The plate was immersed in a contaminant solution to a height of 12.7 ± 0.3 cm. The total surface area immersed was 371 sq. cm.; the 2.4 sq. cm. area on the bottom of the plate was neglected.

The device used to move the plate vertically and horizontally, a small scale model of a metal-finishing rinse dipper, was modified slightly in order to minimize vibrations in vertical motion which had occurred due to wear in previous use.

The contaminant solution was made by dissolving 2.5000 g. of Pontamine blue dye in 1 liter of distilled water; the solution had a density of 1.0025 g./ml. Dilute solutions of this dye were analyzed for concentration using the Evelyn photoelectric colorimeter in the same fashion described earlier (*4*), except that the instrument was recalibrated and a more stable power supply was provided. The calibration curve was sufficiently precise to determine the concentration within 1 to 7% relative error, depending on the concentration used. A majority of the test runs were made at calibration readings such that the relative error was about 2.5 ± 1.5%.

To prepare the plate for measurement it was first cleaned with fine grade 0 Emery cloth; the residue from the Emery cloth was wiped off the plate using cotton balls soaked with a detergent solution. The plate was then submerged into a small trough with running tap water for 15 to 20 min. to wash out the detergent and transferred to a distilled water bath for a second washing. The plate was then mounted on the apparatus. Any dust deposited on the surface during mounting was sprayed off with distilled water. The surface was then dried by spraying with acetone. This procedure of preparing the plate was necessary to insure that it was clean. Experience indicated that if it were not clean, the liquid would not uniformly wet the plate. Only completely wetted plates were studied.

The Freeze Method for Measuring V_B

The freeze method was used to convert all film liquid into a solid form so that the side film and bottom drop could be separated physically.

After many trials and modifications, freezing was successfully accomplished by immersing the plates slowly into a bath of liquid nitrogen (−196°C.). The liquid nitrogen container was made of white styrofoam with inside dimensions of approximately 2.5 cm. wide, 14.5 cm. long, and 15 cm. deep. The container walls were 4 to 5 cm. thick to provide sufficient insulation to prevent nitrogen evaporation at walls.

The immersion process for freezing had to be done at a controlled pace to allow for heat effects. For example, rapid immersion resulted in splattering of the drop and, consequently, loss of the sample.

The speed of immersion was more closely controlled manually than by using the available motor driven apparatus. Therefore movement was done manually. The plate with the adhering film was first held stationary for a moment above the liquid bath. Then contact was made by raising the liquid nitrogen bath.

Figure 1 shows the shape of the bottom drop observed in end-view photographs (*3*). Measurements from the pictures showed that the maximum thickness of the drop at 25 to 400 sec. drain time was the same order of magnitude as the thickness of the plate, i.e. 0.1 to 0.2 cm.

The distinction of a bottom drop from the side film was somewhat arbitrary, as shown in a side view photograph (*3*). However, the boundary between the lower edge of side film and the upper edge of the bottom drop appeared to be a surprisingly sharp demarkation. The relatively distinct demarkation region was due to the colorimetric effect found by comparing thick and thin films containing the same concentration of dye and was therefore called the dye line. The dye line between the bottom drop and the rest of the adhering solution was more obvious after the plate and its dyed liquid had been frozen, as shown photographically (*3*).

Immersion was done in two stages. In the first stage approximately 0.5-0.6 cm. of the plate was slowly submerged to cover the bottom drop; about 10 sec. were required in order to freeze the bottom drop and the immediately adjoining side film. In the second stage the rest of the plate and side film was entirely immersed. In each stage the speed was controlled to minimize the disturbance due to heat of the shape of the bottom drop that from the hot (room temperature) plate. Special precaution was used in the first stage to minimize the effect of convection on the shape of the drop.

After the drop had been frozen the bottom drop was scraped off using a sharp razor blade and collected in a metal container; the experimenter used a rubber glove so any contaminant that stayed on the glove was easily seen

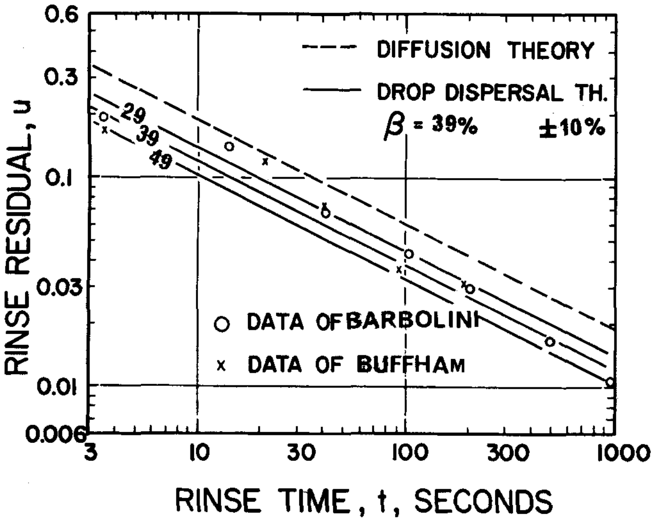

Fig. 4. Comparison of the drop-dispersal theory with rinse data.

and removed by washing. This solid and partly melting mass was diluted by distilled water to a standard volume and its concentration measured. The remainder of the frozen liquid, representing the side film above the bottom drop, was melted by spraying fine streams of distilled water, collected and analyzed in the usual way.

The freeze method provided separate measurements of the bottom drop volume and the side film volume. The total carry-over volume was then obtained by addition. The freeze procedure for measuring the bottom drop volume resulted in runs which were quite reproducible. For example, results for one run were 0.375, 0.371, and 0.376 ml.; in another run 0.575, 0.574, and 0.560 ml. were obtained. Reproducibility varied from ±1 to ±3%. Bottom drop fractions were found to vary considerably (that is 39 to 58%) in the drain time range from 20 to 140 sec.

PART IV. TEST OF THE BOTTOM DROP THEORY

The bottom drop model to be tested is

$$U = \frac{V_c(1-\beta)}{A\sqrt{\pi D t}} \tag{15a}$$

Rinse data of Buffham (*2, 5*) and Barbolini (*1, 6*) were used to test Equation (15*a*). Both used Pontamine blue dye ($D = 0.5 \times 10^{-5}$ sq. cm./sec.), a plate of similar dimensions and immersions to that described above (371 sq. cm. area), a wide range of contact times, and a withdrawal speed of 1.9 cm./sec. For β values, consider Table 1.

TABLE 1. BOTTOM DROP CONDITIONS§

(All with 1.9 cm./sec. withdrawal speed)

Source of Data	Buffham (2)	Barbolini (*1*)	Mattson	This Work Li(*3*)
Journal Reference	(*5*)	(*6*)	(*7*)	—
Drain Time, sec.	20(est)	20(est)	20(est)	20
Temp., °F.	70 to 86	70 to 78	75 to 80	76
Volumes, ml.				
1. Bottom Drop V_B	—	0.41* ±1%	0.13†	0.37‡ ±1%
2. Carryover, V_c	1.00 ±5%	0.89 ±2%	0.71 ±6%	0.97 ±1%
Bottom Drop Fraction, β	—	45%	18%	39%

* Touch method (Believed to be high)
† Scoop method (low)
‡ Freeze method
§ ± values represent reproducibility test results

Rinse residual data are plotted in Figure 4 together with the bottom drop model (using $\beta = 39 \pm 10\%$) and the diffusion model. Noting the four second data (*6*), the log-log slope of U vs t is about $-\frac{1}{2}$.

Figure 4 shows that the bottom drop model is appreciably better than the diffusion model, except perhaps for two runs at 15 to 20 sec. The average deviation between theory and data is reduced from about 45% (for $\beta = 0$) to about 15% (for $\beta = 39\%$) by using the new drop dispersal theory.

There are several uncertainties in the data, however. They include the lack of accurate values of temperature and drain time for the rinse conditions and differences in carry-over volumes (See Table 1). The apparent closeness of the freeze method β with the touch method β is unexpected, but may be due to improper comparison due to uncontrolled parameters. There is some indication that the bottom drop fraction is somewhat higher than the secondary amount actually dispersed, but there are too many tertiary uncertainties present to clarify this possibility.

Some scholars might prefer to lump the observed surface effect of drop dispersal (*5*) into an effective diffusivity *De* and empirically obtain *De*, which would be larger than *D*. Such an approach would mask the observed mechanism of drop dispersal. The authors feel that use of an effective diffusivity for combining convection and diffusion should be used primarily for cases where one is unclear as to mechanism.

In summary, the mixing noted in the data of Figure 4 is due to diffusion (primarily) and convection (secondarily). It appears that the drop dispersal model is useful for quantitatively describing the secondary mixing effects which occur under the conditions studied.

PART V. FILM DISTRIBUTION DATA

The volumetric data obtained using the freeze method are given in Tables 2 and 3 and the bottom drop fraction is shown in Figure 5.

The bottom drop fraction is very sensitive to drain time between 20 and about 100 sec. but asymptotically approaches a constant value somewhere between 100 and 140 sec. The shortest time studied, 20 sec., was the minimum time required to transport the plate from the contaminant bath to the nitrogen bath. Figure 5 indicates that the bottom drop fraction is probably appreciably smaller at drain times less than 20 sec.

The effect of a temperature change of 13°F. was substantial, as shown in Figure 5. The reasons for the sensi-

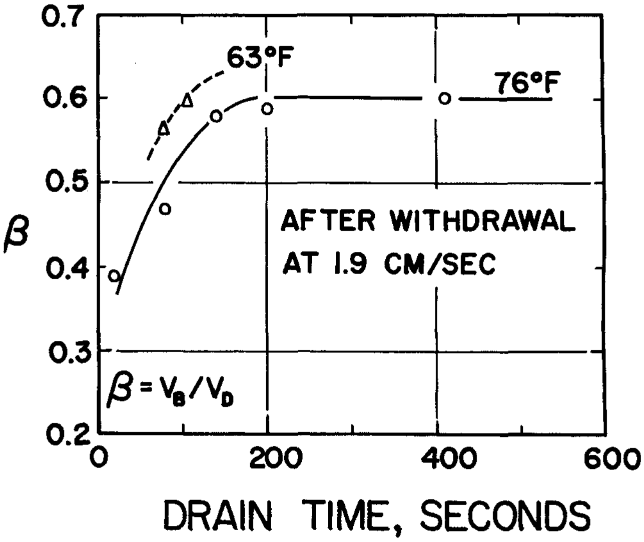

Fig. 5. Effect of drain time on bottom drop fraction.

tive effect of temperature on β are not completely understood. The temperature effect on carry-over volume (Tables 2 and 3) can be explained as due to changes in viscosity as predicted by equations for continuous withdrawal. However, the increase in bottom drop volume with increasing temperature is unexpected based on free *drainage theory;* it may be due to changing profiles in unsteady withdrawal.

Table 2 shows that reproducibility of the carry-over volume was appreciably better than reproducibility of the bottom drop volume. This result indicates the small but noticeable variation in the demarcation line chosen between the bottom drop and the side film. No drippage occurred in any of the runs shown in Tables 2 and 3.

TABLE 2. EFFECT OF TIME ON FILM DISTRIBUTION (76°F.)

Drain Time, sec.	20	80	140†	200	415
Volumes, ml.*					
Bottom Drop, V_B	0.37 ±1%	0.45 ±3%	0.57 ±2%	0.57 ±2%	0.60 ±3%
Side Film, V_s	0.59 ±0.5%	0.51 ±3%	0.41 ±3%	0.40 ±2%	0.40 ±2%
Carry-over, V_c	0.97 ±0.4%	0.96 ±0.2%	0.98 ±0.8%	0.97 ±0.9%	1.00 ±2%

* Average of three determinations. The ± values represent reproducibility measured as average deviations from the mean. Carry-over volumes were taken as the sum of bottom drop and side film volumes.

† 74°F.

TABLE 3. EFFECT OF TIME ON FILM DISTRIBUTION (63°F.)

Drain Time, sec.	80	105
Volume, ml*		
Bottom Drop, V_B	0.61 ±2%	0.66 ±5%
Side Film, V_s	0.47 ±2%	0.44 ±2%
Carry-over, V_c	1.08 ±2%	1.10 ±3%

* See Table 2.

DISCUSSION OF CARRY-OVER

Tables 2 and 3 show that, for a given temperature, carry-over volume is constant. Specifically, the volume was found to be about 0.975 ml. at 76°F. and 1.09 ml. at 63°F. This constancy is expected because no drippage occurred.

The carry-over volume at the lower temperature was about 12% higher than that at 76°F. This effect of temperature is surprisingly close to the 13% predicted by the continuous withdrawal theory (*8*); here the 13% effect was calculated by taking the 2/3 power of the ratio of viscosities, namely 1.083 centipoise at 63°F. and 0.904 centipoise at 76°F.

In order to check quantitative removal of the dye in the freezing method, carry-over volumes were measured in independent tests using the water wash method of previous workers (*4, 5*). The volumes obtained, 1.09 and 1.02 ml. at 63 and 76°F. respectively, indicated good agreement between the two methods.

CONCLUSIONS

1. A theoretical rinsing model which includes the effect of surface drop dispersal and unequal dragout has been developed by extension of the diffusion model. The drop-dispersal theory reduces to three special case theories, including the diffusion model.
2. The drop-dispersal theory was tested for the equal dragout case and found to agree better with data than the diffusion model.
3. The drop-dispersal theory qualitatively predicts the effect of variable carry-over and dragout for the case of unequal dragout.
4. The freeze method was developed, tested, and found suitable for studying transient film distributions.
5. The bottom drop fraction was found to vary significantly with drain time, increasing at one condition from 39% at 20 sec. to an asymptotic value of about 60% after 140 sec.

ACKNOWLEDGMENT

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NOTATION

A = surface area of plate, sq. cm.
C = concentration, g./ml.
D = mass diffusivity, sq. cm./sec.
D_m = function, Equation (8)
L = length or average film thickness, cm.
t = contact time, sec.
x = rectangular coordinate
U = rinse residual, dimensionless, Equation (1)
V = volume, ml.

Greek Letters

β = bottom drop fraction, V_B/V_c
δ = dragout fraction, V_D/V_c
π = 3.14159 . . .

Subscripts

B = bottom drop
c = carry-over
D = dragout
s = side film
T = tank

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