r = radial

s = surface

### LITERATURE CITED

Aris, R., "Introduction to the Analysis of Chemical Reactors," p. 140, Prentice-Hall, Englewood Cliffs, N. J. (1965).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, pp. 245 & 502, Wiley, New York (1960).

Frank-Kamenetzky, D. A., "Diffusion and Kinetics of Heterogeneous Reactions," Acta Physicochim. U.R.S.S., 16, 357 (1942).

Hlavacek, V., and M. Kubicek, "Modelling of Chemical Reactors. XXIII. Transient Heat and Mass Transfer in a Porous Catalyst. III. Reaction with Finite Values of Sherwood and Nusselt Numbers. Effect of Volume Contraction," J. Catal., 22, 364 (1971).

Hlavacek, V., M. Marek, and M. Kubicek, "Modelling of Chemical Reactors: VII. Heat and Mass Transfer in a Particle of Porous Catalyst. Zero-Order Reactions-Numerical Results," Collect. Czech. Chem. Commun., 33 (3), 718 (1968).

Lih, M. M., and Lin, K., "Concentration Profiles and Effectiveness Factor in Catalyst Particles with Reactant-to-Product Volume Change: First-Order Kinetics," J. Chinese Inst. Chem. Engrs., 2(1), (1971).

Lin, K., "Effectiveness Factor in Catalytic Reactions with Volume Change," Ph.D. dissertation, Catholic U. of America, Washington, D. C. (1970).

Washington, D. C. (1970).

——, and Lih, M. M., "Concentration Distribution, Effectiveness Factor, and Reactant Exhaustion for Catalytic Reaction with Volume Change," AIChE J., 17, 1234 (1971).

" "Effectiveness Factor for Catalytic Reactions of Arbitrary Order and with Volume Change," to be published. Parks, J. R., "Criticality Criteria for Various Configurations of a Self-Heating Chemical as Functions of Activation Energy and Temperature of Assembly," J. Chem. Phys., 34, 46 (1961).

Peterson, E. E., Chemical Reaction Analysis, § 4.4 Prentice-Hall, Englewood Cliffs, N. J. (1965).

Weekman, V. W., Jr., "Combined Effect of Volume Change and Internal Heat and Mass Transfer on Gas-Phase Reactions in Porous Catalysts," J. Catal., 5, 44 (1966).

Manuscript received June 13, 1972; revision received February 16 and accepted February 17, 1973.

# Dropwise Condensation Phenomena

Dropwise condensation of water vapor on long vertical tubes was investigated as to in situ cleaning and promoting techniques for a variety of tube materials.

Excess promoter on the tube surface significantly reduces heat transfer but appears to be slowly removed by draining.

Measured steamside heat transfer coefficients for copper, gold, Admiralty, Cu-Ni 90-10, and Monel tubes are adequately correlated by the theory of Mikic (1969) modified to include the effect of wall thickness.

A photographic study revealed that falling drops are elongated into rivulets on long vertical surfaces. Short (<65 mm) rivulets and small, barely visible drops over most of the area are evidence of excellent dropwise condensation.

DAVID G. WILKINS and LEROY A. BROMLEY

Department of Chemical Engineering
University of California
Berkeley, California 94720
and
The Bodega Marine Laboratory
University of California
Bodega Bay, California 94923

# **SCOPE**

Heat transfer can be greatly improved by condensing vapor as discrete drops rather than as a continuous film. Dropwise condensation of water vapor is achieved by applying an organic compound to render the surface non-wetting. Promoter life is short under industrial conditions mainly due to fouling. One of the objectives of this study was to find more effective cleaning and promoting tech-

Correspondence concerning this paper should be addressed to L. A. Bromley. D. G. Wilkins is with U. S. Borax Research, Boron, California

niques for a variety of tube materials, especially the more corrosion-resistant alloys. Testing was done in a single tube apparatus and a five-effect Multiple Effect Flash Evaporator (Bromley and Read 1970).

Steamside heat transfer coefficients with dropwise condensation have been reported by others for copper, zinc, and stainless steel and were found to be dependent upon the thermal conductivity of the tube material. Two disparate theories have been advanced to explain this phenomenon. The validity of these theories was tested by measuring dropwise heat transfer coefficients for a variety of tube materials.

# CONCLUSIONS AND SIGNIFICANCE

Copper, copper alloy, and gold tubes were cleaned and promoted in situ to 100% excellent dropwise condensation. Cuprous oxide and iron oxides were removed from tube surfaces by sulfur dioxide in steam. Stubborn deposits were removed by either chlorine, bromine, or (di-)nitrogen trioxide in steam followed by sulfur dioxide. These gases are very toxic and corrosive and must be used sparingly. Promotion of the tubes to dropwise condensation was accomplished using either tetrakis octadecyl thio silane, n-octadecyl mercaptan, or lauryl mercaptan, all of which are excellent promoters.

Karbate (coated carbon) tubes could be promoted to dropwise condensation only if the impervious coating were removed and the promoter applied to the dry tube surface. Karbate could not be promoted satisfactorily under condensing conditions.

Overall heat transfer coefficients with dropwise condensation were measured as a function of cooling water velocity in the range 2 to 8 meters/second for a variety of tube materials. Steamside coefficients calculated from these overall coefficients showed that the steamside coefficient depended upon the thermal conductivity of the tube material, and, for thin walled tubes, the tube wall thickness. The variation of the steamside coefficient with thermal properties and tube thickness was due to the non-uniformity of metal temperature caused by the presence on the surface of large drops that can be considered inactive. The steamside coefficients were adequately corre-

lated by the theory proposed by Mikic (1969) modified to include the effect of finite wall thickness. Thus the use of dropwise condensation on thin-wall titanium would result in little increase in heat transfer whereas the maximum possible dropwise heat transfer coefficient can be attained on a rather thick-wall (~ 1mm) promoted high conductivity (copper) tube.

Although only a monolayer of promoter was required to attain dropwise condensation many layers were applied during promotion to ensure complete coverage. The thermal resistance of these excess layers was appreciable. The time required for the excess promoter to be removed depends upon the promoter and can require up to seven hours for a 1.8 meter tube. The mechanism of removal of the excess promoter was, most probably, draining by gravity.

The character of high quality dropwise condensation on a vertical surface more than a few centimeters high was different from that previously reported. Falling drops were elongated into rivulets. These rivulets were unstable beyond a certain length to width ratio due to surface forces. With high quality dropwise condensation only short (< 65 mm) rivulets were found. Short rivulets were important because they increased heat transfer by increasing the frequency at which an area of surface was swept clear of drops. The lost tails of the rivulets result in a small number of single randomly spaced moderate sized (1 to 3 mm) drops on the surface.

### PREVIOUS WORK

Bromley et al. (1968) conducted a limited number of tests on copper tubes of promoters, methods of application, corrosion-erosion resistance, etc. The tubes were prepared for promotion by in situ cleaning with sulfur dioxide in steam or, for stubborn deposits, chlorine in steam. The best promoter found was tetrakis octadecyl thio-silane  $[(C_{18}H_{37}S)_4Si]$  which was applied by injecting a 1% solution in octanoic acid into the seawater feed. This promoter had a life of several hundred hours under favorable conditions.

Wilkins et al. (1973) found that in the absence of organic contamination gold condensed water vapor in a filmwise manner. The gold was readily promoted to excellent dropwise condensation with tetrakis octadecyl thio-silane.

The effects of heat-flux, steam velocity, promoter and plate height were found to be small for fluxes less than 0.25 MW/m² and plate heights from 25 to 100 mm by Tanner et al. (1965b) and Le Fevre and Rose (1965). Earlier Shea and Krause (1940) had noted a dependence upon plate height; however, this was probably due to poor quality of dropwise condensation.

Only a monomolecular layer of promoter is required to achieve dropwise condensation. During the application of promoter much more than a monolayer can be accumulated on the surface. The thermal resistance of these excess layers of promoter can significantly reduce heat transfer. Tanner et al. (1965b) reported that one hour was required to remove the excess layer with the promoter dioctadecyl disulfide. Using the same promoter Citakoglu and Rose (1968) found that up to 3 hours were required to remove the excess layers.

The steamside coefficient has been shown to depend upon the thermal properties of the subsurface material. Tanner et al. (1965b) reported a coefficient of 0.24 MW/m<sup>2</sup>°C for copper and 0.034 to 0.045 MW/m<sup>2</sup>°C for

stainless steel, both with the promoter montanic acid. No difference was noted in the appearance of the two surfaces.

Griffith and Lee (1967) reported steamside coefficients for several surfaces in a horizontal position facing down. Their results were coefficients of 0.057 MW/m<sup>2</sup> C for copper, 0.026 MW/m<sup>2</sup> °C for zinc, and 0.011 MW/m<sup>2</sup> °C for stainless steel. Each of these surfaces was identically gold-plated; therefore, these differences cannot have been due to surface characteristics such as nucleating ability. They could only be due to the differences in thermal properties of the subsurface material.

Until recently no theory of dropwise condensation considered explicitly the effect of the thermal properties of the surface material. These effects have been shown to be important. Two recent theories have been advanced to explain this phenomenon. Mikic (1969) treats the problem as essentially steady state while Nijaguna and Abdelmessih (1971) consider transients to be controlling.

# EXPERIMENTAL APPARATUS

The apparatus used in this investigation has been described (Bromley et al., 1968; Wilkins et al., 1973) and consisted of a vertical condenser with an active tube length of 1.42 m housed in 76.2 mm I.D. glass pipe. Water vapor (made from sea water) at one atmosphere condensed on the outside of the tube and distilled water was circulated through the inside in a closed loop. The feed seawater used to generate vapor, had been filtered, pH adjusted, and degassed. Excess brine and the condensate were sent to drain.

Inlet and outlet cooling water temperatures were measured in insulated mixing chambers with Hewlett-Packard quartz thermometers, absolute accuracy  $\pm 0.01\,^{\circ}\mathrm{C};$  in addition thermocouples were used. The cooling water flow was read from a calibrated rotometer. A short-range mercury thermometer was read to  $0.01\,^{\circ}\mathrm{C}$  for the steam temperature.

A detailed description of the apparatus can be found in Wilkins (1972).

TABLE 1. CONDENSER TUBE SPECIFICATIONS

Tube material	O.D., mm	Wall thickness, mm	Thermal conductivity at 93° C
Admiralty alloy 443	15.9	1.24	121 W/m°K
Copper ÓFHĆ alloy 101	15.9	0.89	393
Copper-Nickel alloy 706	15.9	1.24	50
Gold 99.95% pure	15.9	0.89	<b>2</b> 94
Karbate	18.8	3.43	97
Monel	16.0	0.51	27

#### Condenser Tubes

The specifications of the condenser tubes used in this work are listed in Table 1. The thermal conductivity data for the metal tubes were obtained from Touloukian (1970). The thermal conductivity of Karbate was obtained from the Union Carbide Company.

### Cleaning

Condenser tubes must be clean before they can be promoted effectively. The previous technique of using sulfur dioxide and chlorine in steam was found to be effective on copper alloy tubes as well as on copper. The alloy tubes tested were brass, 90-10 copper nickel, and Monel. Bromine or (di-) nitrogen trioxide in steam was also found to clean well. Of the cleaning agents (di-) nitrogen trioxide was the most effective for stubborn deposits; however, it is also the most toxic and caution must be exercised in handling this gas.

Hot, foamy, acidified sea water was found to be moderately effective as a cleaning agent. Loose iron oxide could be removed from the tube surface by foam. Sulfur dioxide also slowly (1 hr.) removed the more adherent iron oxide. The best foamers tested were Alipal CO436† and Joy.†

### **PROMOTERS**

The promoters that worked well for copper and gold were also found to be excellent promoters for Admiralty, 90-10 copper-nickel, and fair for Karbate. There was some variation. Tetrakis octadecyl thio silane was best for copper, 90-10 copper-nickel and gold. The mercaptans *n*-octadecyl and lauryl were better on Admiralty, Karbate, and Monel. A 50-50 mixture of the two mercaptans also appeared to remove the protective film that forms on the arsenical inhibited Admiralty. None of the other cleaning agents were particularly effective in removing this film.

An attempt was made to promote a titanium tube but only very short-lived dropwise condensation could be achieved.

Promotion by vapor phase transfer worked well for all the tubes tested except for Karbate. The technique worked best when the promoter was injected directly into the boiling sea water. Approximately 1 cu. cm. or less of solution was required to promote a single tube.

The Karbate tube could not be promoted in place for more than a few minutes. This is in agreement with the observation of McCormack and Westwater (1965) that graphite particles are extremely poor nucleation sites for drop formation. It was found that if the impervious coating normally present on Karbate was removed by sanding the tube with fine steel wool, dropwise condensation could then be maintained for several minutes by in situ promot-

• Karbate is the trade name of Union Carbide Co. for resin-impregnated graphite.

ing. However, since this was not satisfactory, the Karbate tube was removed from the apparatus and promoter (n-octadecyl mercaptan) was applied directly to the tube surface. This gave good dropwise condensation that lasted several hours. A possible reason for the poor performance of the Karbate was the porosity of the tube since these pores could trap water and hence tend to make the tube more wetting.

Extensive life tests were not conducted on any of the promoters or tubes. General trends were noted. These observations can be summarized as follows for copper and copper alloys:

- 1. Promoter life on a given tube increases with increasing copper content of a tube, reaching a maximum with pure copper.
- 2. Promoter life increases with increasing molecular weight within a class of compounds, for example, thio silanes, mercaptans. Promoter life tends to be longer for the thio silanes than for the mercaptans for the same basic unit.
- 3. Resistance to erosion increases with increasing copper content of tube material.

These observations are consistent with a mechanism that involves the chemical adsorption of the active end of the promoter molecule to the copper atoms of the surface as proposed by Blackman and Dewar (1957).

Promoters on gold and Karbate had a shorter life than on pure copper. On these former materials the promoter is probably physically adsorbed rather than chemically; therefore, a shorter life could be expected.

# OVERALL HEAT TRANSFER COEFFICIENTS

Overall heat transfer coefficients with dropwise condensation were measured for the tubes listed in Table 1. These results are summarized in Figure 1. The coefficients are considered to have an error of from 1 to 3%. Tabular values are recorded by Wilkins (1972) along with some filmwise results.

The promoters used were:

Material Fromoter(s	Material	Promoter	s`
---------------------	----------	----------	----

 $\begin{array}{lll} \mbox{Admiralty} & \mbox{Lauryl} + n\mbox{-octadecyl mercaptan} \\ \mbox{Copper} & \mbox{Tetrakis octadecyl thio silane} \\ \mbox{Copper-nickel 90-10} & \mbox{Tetrakis octadecyl thio silane} \\ \mbox{Gold} & \mbox{Lauryl mercaptan} \\ \mbox{Karbate} & \mbox{$n$-octadecyl mercaptan} \\ \mbox{Monel} & \mbox{Lauryl} + n\mbox{-octadecyl mercaptan} \end{array}$ 

# COMPARISON WITH OTHER REPORTED RESULTS

Overall dropwise heat transfer coefficients for a vertical copper tube have been reported by Hampson (1961) and Bromley et al. (1968). The overall coefficients for gold in Figure 1 were previously reported by Wilkins et al. (1973). No coefficients with dropwise condensation are known to have been reported for the other tube materials.

Hampson (1961) reported overall dropwise coefficients for a 15.9 mm O.D., 0.51 mm wall-thickness, 0.61 m long vertical copper tube. Over the common range of velocities, the present results agree within the experimental error with those of Hampson.

The present results for a copper tube were 40 to 50% higher than those of Bromley et al. (1968). This difference was greater than their experimental error and was probably due to a combination of fouling of the inside tube surface and an unaccounted systematic error in their data.

t Alipal CO436 is an ammonium salt of sulfated monylthenoxypoly (ethylene-oxy) ethanol produced by General Aniline and Film Corp; Joy is a combination of three surfactants (sulfated alkyl ethylene oxide: trialkylamine oxide; alkyl glycerol sulfonate) and is produced by Procter and Gamble Corp.

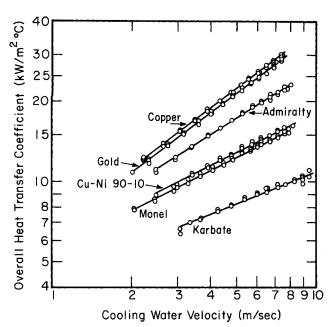


Fig. 1. Overall heat transfer coefficients with dropwise condensation.

### Fouling of the Inside Tube Surface

At the temperatures encountered in these experiments the copper tube will react with the oxygen in the cooling water to form an oxide film that can have a deleterious effect upon heat transfer. This may also be a problem but to a lesser extent with Admiralty and 90-10 copper-nickel.

An easy way to remove this oxide film is to acidify the cooling water to a pH of from 2 to 4. Two methods of acidifying were employed initially, namely adding concentrated HCl batchwise or bubbling  $SO_2$  continuously into the cooling water. The overall heat transfer coefficients obtained with these two methods differed by 10%. The coefficients with  $SO_2$  were the lower ones as shown in Figure 2.

Other tests with SO<sub>2</sub> that were conducted showed that in the absence of oxygen in the cooling water there was no lowering of the heat transfer coefficient. The reduction was probably caused by the formation of cuprous or cupric sulfite both of which are insoluble in hot water but soluble in dilute HCl. This lowering of the heat transfer coefficient with SO<sub>2</sub> was quite reproducible although, if there were no initial oxide film on the tube, a few hours were required due to the slow rate of oxygen transfer to the cooling water. The coefficients rose quickly when the SO<sub>2</sub> was replaced with HCl.

### STEAMSIDE COEFFICIENTS

The surface temperature of thin-wall tubes cannot be measured accurately under condensing conditions. An indirect method was developed, therefore, to calculate the steamside coefficients. This method has been described by Wilkins et al. (1973) and basically was the Wilson method modified to account for the uncertainty in the experimental data and in the correlation for the inside coefficient. The steamside coefficients calculated in this manner are listed in Table 2. These values are considered to be the lower confidence limit on the true value at the 95% confidence level.

# Factors That Can Influence the Steamside Coefficient Noncondensables

The steamside coefficient with dropwise condensation has been shown to be quite sensitive to the noncondensable gas concentration in the steam. Le Fevre and Rose (1965) reported that simply blowing off steam was ineffective in removing noncondensables even if done for several hours. Placing a vent near the condensing surface was necessary to adequately remove inerts in their closed system.

Tanner et al. (1965a) found the effects of noncondensables could be eliminated by having a low (2 ppm) noncondensable gas concentration in the steam, condensing only a small (15%) fraction of the total steam flow and maintaining a high steam velocity across the condensing surface.

The precautions taken to eliminate noncondensables in the present investigation were those normally employed in a seawater conversion plant. The dissolved oxygen content of the seawater feed was measured by Sridhar (1972) and found to be 35 to 45 ppb. Nitrogen is twice as soluble in

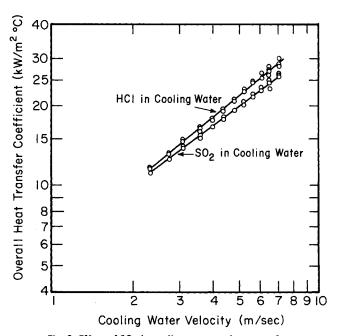


Fig. 2. Effect of SO<sub>2</sub> in cooling water on heat transfer.

Table 2. Observed and Predicted Steamside Coefficients with Dropwise Condensation

	$h_o$ observed		$h_o$	$h_o$	$h_o$ with thickness
Material	B.t.u./hr-ft <sup>2</sup> °F	(MW/m²-°C)	transient	constriction	dependence
Copper Gold	40,000	0.226	0.226*	0.216	0.216
Gold	35,000	0.199	0.167	0.205	0.204
Admiralty	28,000	0.159	0.122	0.158	0.174
Cu-Ni 90-10	22,000	0.124	0.079	0.103	0.119
Monel	9,700	0.055	0.070	0.070	0.050

<sup>• 0.226,</sup> the value for copper, was arbitrarily chosen as the reference value for calculations of he for the transient theory.

seawater as is oxygen for a total noncondensable gas concentration in the steam of at most 0.28 ppm. A minimum of 10 to 20% of the total steam flow passed completely through the active condensing section to the auxiliary condenser as shown by Bromley et al. (1968). Noncondensables should not have affected the steamside coefficients in the present investigation.

### **EXCESS PROMOTER**

The rates of removal of some of the promoters used in this study were determined. This was accomplished by adding excess promoter to a copper tube that had been condensing dropwise for several hours. The effect of this excess promoter on the overall heat transfer coefficient was observed. The result of adding 1/4 cc of a 50-50 mixture of lauryl and n-octadecyl mercaptan is shown in Figure 3. The overall coefficients required five to seven hours to return to their previous values. When lauryl mercaptan alone was tested, heat transfer was reduced for 30 to 45 minutes.

The decreased heat transfer after adding excess promoter appears to be caused by the thermal resistance of the excess promoter as was suggested by Citakoglu and Rose (1968). The mechanism of promoter removal was not clear.

A few calculations showed that promoter distilled rapidly from the sea water boiler and was nearly quantitatively transferred to the condensing surface and that neither dissolution nor evaporation appeared to be the mechanism of removal.

The most likely mechanism seems to be draining due to the forces acting on the film. These forces were gravity and viscous drag of the falling drops. Using an equivalent film thickness based on heat transfer measurements an apparent viscosity was calculated for the promoter *n*-octadecyl mercaptan using the draining equation of Van Rossum (1958). The result was an apparent viscosity of 5 cp. This was a reasonable value and indicates draining was the most probable mechanism of promoter removal.

# SURFACE THERMAL PROPERTIES (TRANSIENT THEORY)

Nijaguna and Abdelmessih (1971) have proposed a model of dropwise condensation that considers the precoalescence life of a drop to be the limiting factor. Their model approximated the growth of a precoalescence drop by the transient conduction through a composite slab, one slab (the drop) of finite thickness in contact with a semi-infinite slab and no contact resistance. Their final expression for the average steamside coefficient was

$$h_0 \propto rac{4}{3} \, N_d \, igg( rac{k}{\sqrt{\pi lpha_s t}} \, igg)$$

where  $N_d$  was the active drop density. This expression is not dimensionally consistent. To be correct the right hand side should be multiplied by the area covered by one drop.

This model predicted that the steamside coefficients should vary as the group  $(k_s/\sqrt{\alpha_s})$  that is  $(\sqrt{k_s\rho}C_p)$ . This model was based on the transient part of the solution to the conduction problem. Before applying this prediction one should ascertain that the steady state part of the solution can be neglected. This is equivalent to finding that the response time of the metal surface is long as compared to the precoalescence lifetime of a drop. This was not considered by Nijaguna and Abdelmessih (1971).

Using the results of Heasley (1965) for the response time of the metal surfaces, the average maximum pre-

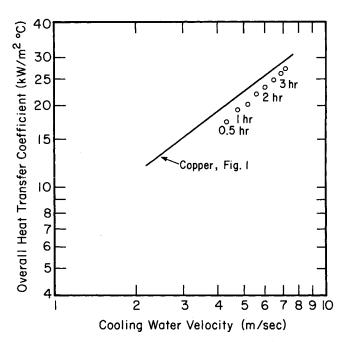


Fig. 3. Effect of excess promoter on heat transfer.

coalescence drop size determined by McCormick and Westwater (1966), and kinetic theory for maximum growth rate the response time and precoalescence lifetime were calculated. For a copper surface the response time was two orders of magnitude smaller than the precoalescence lifetime. For titanium the response time was one order of magnitude smaller.

Thus the heat flux capacitance does not appear to be significant in dropwise condensation. This theory also does a poor job of correlating the experimentally observed coefficients from the present work as also shown in Table 2.

# Constriction Resistance Theory

Mikic (1969) considers the differences in the observed steamside coefficients to be due to the nonuniformity of the surface temperature with dropwise condensation caused by the presence of large inactive drops on the surface. The effect of thermal conductivity is to change the degree of surface temperature nonuniformity.

The local vapor-to-surface resistance is highly nonuniform over the dropwise surface. On bare areas and at the edges of drops condensation is rapid, while there is little condensation on the center portion of large drops. Thus the heat flux is nonuniform over the surface. For a surface with a finite thermal conductivity the local temperature then will depend upon the local heat flux. A higher heat flux implies a higher temperature.

The condensing surface can be divided into an inactive area and an apparent effective area. The inactive area would be the area covered by large drops. Welch and Westwater (1961) found that 97% of the heat load was transferred through drops smaller than 0.25 mm diameter and no important conduction takes place on drops large enough to be seen by the naked eye. These small drops comprise the effective area.

The dropwise process was then represented by an elemental heat channel of radius b. An adiabatic disk of radius c placed on one end of the channel represented the inactive drop. The boundary conditions were uniform flux over the effective area  $\pi(b^2-c^2)$  and uniform flux over the total area  $(\pi b^2)$  of the other end of the infinitely long channel. There was no heat loss from the other sides of the channel.

The effect of the adiabatic disk on heat transfer to the

elemental heat channel was to introduce another resistance, the amount being inversely proportional to the thermal conductivity of the channel for a fixed geometry. Mikic (1969) terms their resistance the constriction resistance and the relation for two surfaces, I and II, was

$$\frac{(R_s)_I}{(R_s)_{II}} = \frac{k_{II}}{k_I} \tag{2}$$

The steamside heat transfer coefficient was expressed as the sum of two resistances:

$$h_0^{-1} = R_0 + R_s \tag{3}$$

The resistance  $R_s$  was the constriction resistance and  $R_0$  was the remaining resistance and was constant for all surfaces.

The problem of constriction resistance has been treated as a steady state problem and the distribution of drops on the condensing surface was assumed to be stationary. This is true in the statistical context of the word stationary. As was shown in the preceding section, the transient response of the surface was small compared to the life cycle of an area of the surface, thus the assumption of steady state was justified. Using Equations (2) and (3) with copper as the reference substance and the experimental values of  $h_0$ , a best value of  $R_0$  was calculated by the method of least squares. The resulting calculated  $h_0$  values for the constriction theory are also shown in Table 2.

Mikic (1969) uses this theory to correlate the experimental results of Griffith and Lee (1967) and Tanner et al. (1965b) for copper and stainless steel. This was not proof of the validity of the theory since there were only two experimental materials. This theory is inadequate to predict the third experimental coefficient (zinc) of Griffith and Lee (1967).

## **Effect of Finite Tube Wall Thickness**

In the development of this constriction resistance theory Mikic assumes an infinitely long heat channel. This length was necessary to allow the heat flux to become uniform across the channel. The tube used in the present work cannot be assumed infinitely thick. Many of the drops were several times larger than the thickness of the tube wall. The effect of assuming an infinitely thick heat channel is to underestimate the magnitude of the constriction resistance.

The heat flux in the tube wall will be nonuniform under the large inactive drops and at the cooling surface. A constriction resistance will be created at this cooling surface in the same manner as the one at the condensing surface. Its magnitude will in general depend upon the wall thickness, drop size, distribution, and cooling wall coefficient. As a first approximation these effects can be taken as a function of wall thickness alone. This function can be used to modify Mikic's (1969) expression, giving

$$\frac{(R_s)_I}{(R_s)_{II}} = \frac{k_{II}}{k_I} \cdot f(Z) \tag{4}$$

where Z is wall thickness. The present results were correlated using

$$f(Z) = \frac{Z_{II}}{Z_{I}} \tag{5}$$

The correlated results using Equations (3), (4), and (5) again with copper as the reference substance are shown in the last column of Table 2. Including the thickness dependent term results in a somewhat better fit of the experimental results and indicates there is an additional resistance that should be considered in dropwise condensation with thin-walled tubes.

### Other Evidence for Thickness Dependence

Hurst and Olson (1972) measured the temperature of the underside of a 0.025mm thick copper horizontal foil which had dropwise condensation on the upper side. The foil was cooled by high velocity air. Infrared radiometry was used to measure the temperature over an area about 0.8 mm in diameter. The temperature of the underside of the foil under the center of large drops was found to be appreciably cooler than under the edge of the drop or under small drops.

Hurst and Olson (1972) also present analytical solutions for the temperature profile in the copper plate under a growing drop. From this solution they predict that for either very small drops or a comparatively thick condensing surface the base of the drop can be taken as isothermal. For a drop diameter of 2.5 mm, a copper surface 0.125 mm thick would be sufficient, they predict, to make the base of the drop isothermal. Clearly, if this were true there should be no thickness dependence in the present results for the steamside coefficients.

The results of Griffith and Lee (1967) were taken with specimens gold plated to a thickness of 0.125 mm. Their results showed a definite effect of subsurface thermal conductivity. The analytical model of Hurst and Olson (1972) does not appear to be valid except perhaps for an air-cooled foil which has a very low heat transfer coefficient to the air. With such a low coefficient lateral conduction is more important than conduction through the foil. In the present work the inside coefficients were 2 to 3 orders of magnitude greater. In such a case the base of a drop large enough to be considered inactive cannot be taken as isothermal.

### PHOTOGRAPHIC STUDIES

A high speed and a still photographic study was made of the characteristics of dropwise condensation on a long vertical surface. The situation on a long vertical surface was found to be significantly different from that previously reported. This is illustrated by Figure 4. There are several striking characteristics shown in this photograph. The moving drops were elongated into rivulets. A maximum length of 65 mm was attained by these rivulets. The width of the head of a rivulet was found to increase as the 0.2 power of rivulet length.

These moving rivulets were unstable and broke up by the loss of a tail fragment. In many cases the tail fragments slowed down and became stationary drops. These stationary drops were quite interesting in that they were too large to have grown in place by coalescence. Several of these drops can be seen in Figure 4. Viewing the tube in situ the source of these drops was a mystery. The mechanism of tail fragment loss was established from the high speed studies. Tail fragments in various stages can also be seen in Figure 4.

The mechanism causing the break up of these rivulets was surface tension instability. With excellent dropwise condensation only short rivulets were found. As the quality of the dropwise (contact angle) decreases, the rivulets become longer and eventually form standing streams such as reported by Shea and Krause (1940). This was due to the stabilizing effect of viscous forces at the solid-liquid interface which makes it difficult for the distant edges of a fragment to draw together by surface forces. As the rivulet lengths increase, the rivulets tend to break at random places rather than just at the tail. In that case the fragments tend to be large and to keep moving. Kawai and Kamo (1966) reported the formation of rivulet lengths of up to 100 mm being attained on a 0.3 m plate. When these rivulets broke the fragments remained in motion.

The variation of the fractional area covered by moving

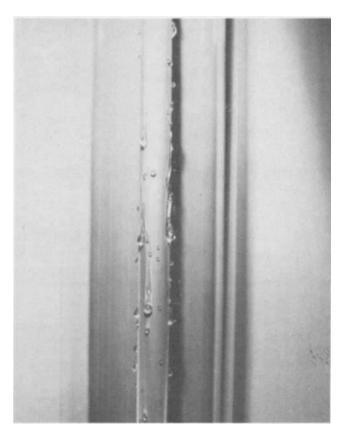


Fig. 4. Character of dropwise condensation on a long vertical surface.

drops with heat flux for plate heights of from 25 to 100 mm was investigated by Rose (1967). For the fluxes encountered in the present investigation Rose (1967) predicted a fractional coverage by moving drops of 0.02. The rivulets on long vertical tubes were found to cover up to 20% of the area. Since the heat transfer coefficient remains high, the increased coverage by moving drops must be compensated by the increased sweeping frequency of these short rivulets. Condensation was rapid on the bare areas exposed by these rivulets as can be seen by the disappearance of a track a short distance behind the rivulet. With a poorer quality of dropwise condensation the rivulets were longer and tended to remain stationary. This reduced both the sweeping frequency and heat transfer as was reported by Shea and Krause (1940).

## **ACKNOWLEDGMENT**

The authors received support for this study from the University of California Water Resources Center.

# NOTATION

= radius of elemental heat channel h

 $C_p$ = specific heat of the solid

 $\boldsymbol{c}$ = radius of adiabatic disk on elemental heat channel

= steamside heat transfer coefficient

k= thermal conductivity

 $k_s$ = thermal conductivity of the solid

= drop density

= heat flux

= thermal resistance in dropwise condensation not including the resistance in the surface

 $R_s$ constriction resistance

= average surface temperature = average vapor temperature

= time

= wall thickness

= thermal diffusivity of the solid

= density of the solid

### **Conversion Factors**

 $1.0 \text{ W/m-}^{\circ}\text{K} = 0.5779 \text{ B.t.u./hr-ft-}^{\circ}\text{F}$ 

 $1.0 \text{ MW/m}^2 = 0.317 \times 10^6 \text{ B.t.u./hr-ft}^2$ 

 $1.0 \text{ MW/m}^2-^{\circ}\text{C} = 0.176 \times 10^6 \text{ B.t.u./hr-ft}^2-^{\circ}\text{F}$ 

### LITERATURE CITED

Blackman, L. C. F., and M. J. S. Dewar, "Promoters for the Dropwise Condensation of Steam," J. Chem. Soc. (London), 162 (1957)

Bromley, L. A., J. W. Porter, and S. M. Read, "Promotion of Drop-By-Drop Condensation of Steam from Seawater on a Vertical Copper Tube," AIChE J., 14, 245 (1968).
———————, S. M. Read, "Multiple Effect Flash Evaporator," Desalination, 7, 343 (1970).

Citakoglu, E., and J. W. Rose, "Dropwise Condensation-Some Factors Influencing the Validity of Heat-Transfer Measurements," Intern. J. Heat Mass Transfer, 11, 523 (1969).
Griffith, P., and M. S. Lee, "The Effect of Surface Thermal

Properties and Finish on Dropwise Condensation," ibid., 10,

697 (1967). Hampson, H., "The Condensation of Steam on a Tube with Filmwise or Dropwise Condensation, and in the Presence of a Non-Condensable Gas," Intern. Develop. Heat Transfer.

Part II, 310 (1961).

Heasley, J. H., "Transient Heat Flow Between Contacting Solids," Intern. J. Heat Mass Transfer, 8, 147 (1965).

Hurst, C. J., and D. R. Olson, "Conduction Through Droplets During Dropwise Condensation," Trans. ASME J. Heat Transfer, 95, Ser. C, No. 1, 12 (1973).

Kawai, T., and N. Kamo, "Study on Application of Dropwise Condensation to Steam Condensation," Bull. J S.M.E., 9, 756 (1966)

Le Fevre, E. J., and J. W. Rose, "An Experimental Study of Heat Transfer by Dropwise Condensation," Intern. J. Heat

Mass Transfer, 8, 1117 (1965).

McCormick, J. L., and J. W. Westwater, "Nucleation Sites for Dropwise Condensation," Chem. Eng. Sci., 20, 1021 (1965). "Drop Dynamics and Heat Transfer During

Dropwise Condensation of Water Vapor on a Horizontal Surface," AIChE Symp. Ser., No. 64, 62, 120 (1966).

Mikic, B. B., "On Mechanism of Dropwise Condensation,"

Intern. J. Heat Mass Transfer, 12, 1311 (1969). Nijaguna, B. T., and A. H. Abdelmessih, "Precoalescence Drop Growth Model for Dropwise Condensation: Influence of Condensing Surface Properties on Precoalescence Drop Growth," A.S.M.E. Paper No. 71-WA/HT-47 (1971).
Rose, J. W., "On the Mechanism of Dropwise Condensation,"

Intern. J. Heat Mass Transfer, 10, 755 (1967).

Shea, F. L., and N. W. Krause, "Dropwise and Film Condensation of Steam," Trans. Am. Inst. Chem. Engrs., 36, 436 (1940)

Sridhar, S., Univ. Calif., Berkeley, private communication to author (1972).

Tanner, D. W., C. J. Potter, D. Pope, and D. West, "Heat Transfer in Dropwise Condensation—Part I., The Effects of Heat Flux, Steam Velocity and Non-Condensable Gas Concentration," Intern. J. Heat Mass Transfer, 8, 419 (1965a).

"Heat Transfer in Dropwise Condensation-Part II. Surface Chemistry," *ibid.*, **8**, 427 (1965b).

Touloukian, Y. S. (ed.), Thermophysical Properties of Matter, the TPRC Data Series Vol. 1., IFI/Plenum, N. Y.—Washington (1970).

Van Rossum, J. J., "Viscous Lifting and Drainage of Liquids," Appl. Sci. Res., A.7, 121 (1958).

Welch, J. F. and J. W. Westwater, "Microscopic Study of Dropwise Condensation," Intern. Develop. Heat Transfer, 302 (1961).

Wilkins, D. G., "Dropwise Condensation Phenomena," Ph.D. Thesis, Univ. Calif., Berkeley (1972).

—, L. A. Bromley, and S. M. Read, "Dropwise and Filmwise Condensation of Water Vapor on Gold," AIChE J., 19, 119 (1973).

Manuscript received February 6, 1973; revision received March 27 and accepted April 6, 1973.