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THE EFFECT OF COATINGS AND SURFACES ON DROPWISE CONDENSATION

By

S. C. Garg, Ph.D.

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NAVAL CIVIL ENGINEERING LABORATORY
Port Hueneme, California 93041

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S. C. Garg, Ph.D.

ABSTRACT

A literature survey of the published information on the effect of coatings and surfaces on dropwise condensation has been carried out. The survey has shown that research to date in promoting dropwise condensation has been limited mostly to small scale laboratory experiments. There appears to be a serious lack of data on methods of application of various dropwise promoters, useful life of promoters, effective concentration, and frequency of promoter renewal. This lack of information is highlighted by the total absence of dropwise condensation as a factor in design of condensers in industry.

Recommendations are made to initiate an experimental program to evaluate the effects of vibrating the condenser surface upon dropwise condensation and the coefficients of heat transfer.

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CONTENTS

	Page
INTRODUCTION	1
MECHANISM OF HEAT TRANSFER IN DROPWISE CONDENSATION	2
LITERATURE SURVEY	7
Criteria for Dropwise Condensation	7
Dropwise Condensation Using Permanent Coatings	8
Dropwise Condensation Using Organic Promoters	12
Increased Heat Transfer Rate by Mechanical Wiping	24
Effect of Condenser Surface	25
COMMERCIAL APPLICATIONS OF DROPWISE CONDENSATION	27
Full Scale Tests	27
Effect of Corrosion Inhibitors	28
Requirements for Practical Use of Dropwise Condensation	28
CONCLUSIONS	29
RECOMMENDATIONS	31
REFERENCES	32
NOMENCLATURE	36
FIGURES	38

INTRODUCTION

In power generating systems utilizing steam (e.g., electrical generation, ship's propulsion, and nuclear power reactor applications), the steam leaving the power unit is reconverted into water in a condenser designed to transfer heat from the steam to the cooling water as rapidly and as efficiently as possible.

The mode of condensation of water vapor in these condensers is important since it determines the efficiency of the condenser. There are two clearly distinguishable ideal modes of condensation, namely (1) filmwise - where the condensate forms a continuous film on the condensing surface, and (2) dropwise - where the condensate is in the form of small drops which are segments of spheres similar in shape, but differing in size. In practical condensers, however, the condensate is usually distributed over the cooled surface in an irregular manner in which some areas approximate dropwise condensation and others filmwise condensation. This mode is generally described as mixed condensation.

There is considerable advantage in preserving dropwise condensation, particularly when large heat transfer rates are desired, since the vapor to condensing surface heat transfer coefficient is of the order of 10 times that for filmwise condensation, and the "overall" coefficient of heat transfer is 2 to 3 times that for filmwise condensation. Increased rates of heat transfer in dropwise condensation may be ascribed to (1) the conduction of heat through the surfaces of drops being greater than that through an equal quantity of liquid spread as a uniform film over the same surface area, (2) the more rapid removal of liquid from the condensing surface in drop form due to coalescence, and (3) the high heat transfer rate through the exposed area between the drops or through the very small drops.[1]

Considerable work has been carried out during the past 35 years or so in devising methods for initiating and maintaining dropwise condensation. Recent technological advances (e.g., space power systems and saline water conversion) have brought about a renewed and vigorous interest in the phenomenon of dropwise condensation. In these cases as contrasted with more conventional systems, the resistance to heat transfer provided by the condensing steam is a significant part of the total resistance so that an increase in the steam side coefficients can have a measurable influence on the overall efficiency of the system. In a large desalination plant, for example, approximately 50% of the expense is in the heat exchanger area and associated equipment, and an increase in the heat transfer efficiency would result in a considerable saving both in investment and in annual operating cost. Therefore, if methods could be devised to promote and maintain dropwise condensation continuously

for an indefinite period of time, the increased heat transfer rates could be translated directly into a proportionate reduction of space, weight, and the cost of condensing equipments.

Various system variables such as heat flux, vapor pressure, surface temperature, surface finish, nature of surface and wettability, presence of impurities and noncondensible gases, vapor velocity, surface orientation, thermodynamic and transport properties of the condensing vapor, and presence of dropwise condensation promoters affect the coefficients of heat transfer in dropwise condensation. This report details the findings of a comprehensive literature survey carried out to determine the effects of coatings and surfaces on dropwise condensation.

MECHANISM OF HEAT TRANSFER IN DROPWISE CONDENSATION

Prior to discussing the effect of coatings and surfaces on coefficient of heat transfer in dropwise condensation, it will be appropriate to discuss various theories on the mechanism of dropwise condensation. It has been accepted by all investigators that the heat transfer rates in dropwise condensation are much higher than those in filmwise condensation under otherwise identical experimental conditions. However, there is a great deal of disagreement upon the precise mechanism by which drops of condensation originate. There are two widely different theories proposed in the past, along with a number of variations of these two theories as explanations of the formation of the droplet

The first main theory was proposed by Jakob[2] in 1936 which may be summarized as follows. The high heat transfer or condensation rate in dropwise condensation is due to a direct contact of the dry cooling surface with hot steam impinging upon it. The condensing steam covers the cooling surface forming a thin layer of water which continually and quickly grows in thickness until it fractures to form droplets. This thickness varies between zero and a small value δ. As the drops coalesce and roll off the surface, a portion of dry surface is exposed and almost instantaneously covered by condensation of fresh steam such that the process repeats itself. For a given steam condition, the average thickness of this layer will depend mainly upon the behavior of the nuclei initiating the condensation, upon the surface, and slightly upon the rate of cooling. If the cooling rate is high (e.g., using a high vapor to surface temperature drop), the drops of a given size are developed by a layer of a given thickness but in shorter intervals of time and surface area. In this case, greater cooling effect is brought into and through the layer, more steam condenses and more drops form, all without changing the average thickness of the layer. The temperature drop across a layer of this kind was assumed to be the same as predicted by the Nusselt theory for filmwise condensation. However, the experimental results enable one

to compute two limiting values for the average film thickness, δ. From the basic equations of heat transfer,

$$Q = h\ \Delta T \tag{1}$$

where h = coefficient of heat transfer, Btu/hr ft^2 ^oF

Q = rate of heat flow, Btu/hr

and ΔT = vapor to surface temperature difference, ^oF

and for heat conduction through a plane layer,

$$Q = k\ \frac{\Delta T}{\delta} \tag{2}$$

where k = thermal conductivity of the condensate, Btu/hr ft ^oF

we obtain:

$$\delta = k/h \tag{3}$$

Using the measured value of h = 14,000 Btu/hr ft^2 ^oF, and assuming the layer to consist of steam (k = 0.0137 Btu/hr ft ^oF), the mean layer thickness would be:

$$\delta \approx 0.98 \times 10^{-6}\ \text{ft} \qquad (\approx 0.0003\ \text{mm})$$

corresponding to about 1,000 diameters of a molecule, this being a very thin layer, since the molecules have a greater distance between them in the steam. If, on the other hand, the layer should consist of water in liquid form (k= 0.40 Btu/hr ft ^oF), its mean thickness would be:

$$\delta = \frac{0.4}{14{,}000} = 28.6 \times 10^{-6}\ \text{ft} \qquad (\approx 0.009\ \text{mm})$$

In view of the above two limiting values, the thickness δ may be considered to be of the order of 0.001 mm. In accordance with this, a film such as Nusselt's is assumed to exist, but the following essential differences. Nusselt's film is a stable layer of continually increasing thickness whereas the layer suggested by Jakob is unstable and changes quickly, but is of a constant mean thickness. The thickness of Nusselt's film depends on the rate of cooling, the height of the cooling surface, etc., whereas the thickness of the Jakob's layer in dropwise condensation depends on the properties of the surface, the purity of steam, etc. Only the rapidity with which new layers originate depends on the intensity or rate of cooling.

The second main theory of dropwise condensation was offered by Emmons[3] in 1939. He suggested that the molecular processes of evaporation,

condensation, and reflection of molecules at surfaces, studied in connection with catalytic and electronic emission phenomena, can be applied in a qualitative way to dropwise condensation.

Consider a vapor in contact with a surface maintained at a lower temperature than the vapor. When the rate of arrival of vapor molecules exceeds the rate of their evaporation from the surface, there is a net accumulation of molecules on the surface. Before the vapor molecules have completely covered the surface, some vapor molecules will arrive on top of the first layer. These will arrive at the same rate as before, but, since the range of atomic forces is extremely small, the rate of evaporation will depend on whether the vapor molecules have a greater or lesser affinity for each other than for the cooling surface.

When the surface has an equal or greater affinity for the vapor molecules than the vapor molecules have for each other, the molecules accumulate faster in the first layer than in the second and third layers, and so on. The cooling surface soon becomes completely covered by a layer of condensed molecules. In order for more layers to form, the latent heat must now be conducted through the layer already present. Finally, as the number of layers became large, they slip over each other due to gravity, and the condensate thus flows off without exposing the cooling surface. This is filmwise condensation.

On the other hand, when the surface has less affinity for the vapor molecules than they have for each other, the second, third and subsequent layers of molecules form before a first layer is completely built. The condensed molecules gather into drops, which grow until their weight becomes sufficient to move them over the surface. Since the adsorption force between the first layer and the surface was assumed to be smaller than the mutual attraction, these molecules are pulled from the cooling surface when the drop moves downward, leaving behind a bare surface upon which the process can repeat itself. This is dropwise condensation.

According to Emmons, the space between the drops is bare in dropwise condensation and the surface has an important effect on the phenomena. The vapor molecules condense on striking the bare cooled surface and are therefore at a lower temperature than saturated vapor. The importance of the process of reevaporation is shown approximately by the equation for the rate of arrival of vapor molecules at the surface as given by the kinetic theory of gases. The rate of condensation of saturated vapor at a pressure of 1-inch of mercury absolute would be 3150 lbs/hr ft^2 if there were no reevaporation. This is roughly 300 times as great as normally used in power plant condenser practice.

According to Emmons, therefore, there must be a blanket of supersaturated vapor covering the bare cooling surface between the drops. Wherever this supersaturated vapor comes into contact with the surface of a drop, condensation occurs very rapidly. A local pressure reduction

takes place which, in turn, sets up local eddy currents in the vapor between the drops. This mechanism is responsible for the very high heat transfer coefficients in dropwise condensation.

There is a serious disagreement between the above two theories of dropwise condensation. Nagle commented on Emmon's theory as follows. The common experience of every man when he takes a bath is pertinent to dropwise condensation. When he is in the water and he gets up, the film breaks almost at once and he is covered with drops. Therefore, he cannot have any supercooled steam or any reevaporation on him. The sheet of water breaks and draws up into drops due to the oily nature of the surface rather than that the water that is deposited as condensate and is reevaporated. In addition, one would expect that reevaporation of condensate and subsequent condensation on the surface of the drops would result in an abnormally low heat transfer rate rather than the very high one found experimentally. The Emmon's mechanism is also in contradiction to that proposed by Eucken[4] earlier. Eucken proposed that liquid nucleation occurs in a thin layer of supersaturated vapor next to the surface, and that in this layer there is a flow towards the drops because of a density gradient created by condensation on the surface of the drops.

In contrast to criticisms of Emmon's theory, Jakob's theory has obtained support from a microscopic study of dropwise condensation conducted by Welch and Westwater.[5] The authors took high speed motion pictures during dropwise condensation on three different, vertically aligned, condensing surfaces. Dropwise condensation was induced by adding 0.005 weight percent cuprice oleate to the feed water in the steam-supply boiler. Steam to surface temperature drops varied from 0.4 to 47°F and the heat flux varied from about 5,000 to 85,000 Btu/hr ft^2. Their photographs showed that dropwise condensation takes place preferentially on the swept regions and only slightly on the drops. The film which then forms on the swept regions builds up to an estimated critical thickness of about 0.5 micron before fracturing to form new drops. The creation of essentially a "bare" surface between drops provided the explanation of high heat transfer coefficients obtained in the dropwise condensation process.

The motion pictures[5] showed that the drops were segments of spheres and had contact angles of $72^\circ \pm 8^\circ$. Numerous coalescences were observed to take place between microscopic drops. Whenever two or more drops coalesced, a part of the metal surface previously covered by the drops was exposed, and a distinct flash of light from the lustrous bare metal was evident. Fresh steam condensed quickly on the cold surface until the luster was lost, indicating the presence of liquid. Shortly thereafter, tiny new droplets became visible. At their first appearance, the drops were considerably smaller than 0.01 mm and thus were too small to permit accurate diameter measurements. At low heat fluxes, the lustrous bare area was visible for a longer period of time compared to that at

high heat fluxes. The time for the first appearance of drops in a bare area was found to be a function of ΔT but not a function of the size of the area. A definite interdependence of the steam to surface ΔT, average heat flux, and the number of coalescences per unit area per unit time was noted. As heat flux was increased, the heat transfer per coalescence decreased, the bare area exposed per coalescence became smaller, and the number of coalescences between small drops increased. The drops grew faster and the frequency at which the drops became big enough to roll down the surface in response to gravity increased. A large number of small drops appeared in the swept path. The study indicated that about 80% of the heat transfer occurred at the bare areas and in the thin liquid film which form on the bare areas.

Based upon the above observations, the authors proposed the following equation to predict the average steam side heat transfer coefficient.

$$h = \frac{\rho\lambda\, X_c}{t_c\, \Delta T} \cdot \frac{A_B}{A_T} \qquad (4)$$

where ρ = density of liquid, lb/ft^3

λ = enthalpy difference between the vapor and the condensed liquid, Btu/lb

X_c = critical film thickness at fracture, ft

t_c = critical time for film growth, hr

A_B = condenser area free of discrete drops, ft^2

and A_T = total area of the condenser surface, ft^2

The values of X_c and A_B/A_T will depend on the properties of the liquid, the solid, and the promoter. Since the local metal surface must show temperature fluctuations as drops form, coalesce, and roll off, the local ΔT is not constant, and varies between zero and a maximum value. In the experimental program, the average values of h and ΔT were measured experimentally and that of t_c obtained from the motion pictures.

Their conclusions may be summed up as follows. For water condensing on copper in a dropwise fashion, the condensation directly on droplets is insignificant for all drops big enough to be seen. The condensation occurs primarily between drops. The region between drops contain a liquid film which builds up in thickness from zero to the critical value at which time it fractures spontaneously to form new drops and newly exposed bare areas. The bare areas cause growth of a new layer which

fractures again after reaching the critical thickness. Whenever a film fractures, the drops on its periphery gain liquid by coalescing with some of the fractured liquid film. At a ΔT of $2^{o}F$, as many as 1000. coalescences in series were observed in the films which resulted in one final drop of about 2 mm diameter after about 7 seconds.

In contrast with the above film fracture theory, Umur and Griffith[6] concluded from a recent investigation of dropwise condensation that a film no greater than a monolayer thick can exist in the area between drops. This finding is based on both theoretical considerations from a thermodynamic point-of-view and on an optical study. The optical study involved determining film thickness by noting changes in the ellipticity of plant polarized light when reflected from the metallic condensing surface. These investigators also proposed a model for drop growth which is consistant with experimentally observed values at atmospheric pressure and at lower pressures which have shown that growth rate is a function of vapor pressure.

McCormick and Westwater[7,8] and Peterson and Westwater[9] considered the initial formation of drops to be the principal mechanism in dropwise condensation. They investigated[7] the identity, behavior, and effective range of nucleation sites during dropwise condensation. Furthermore, using photographic techniques,[8] they found that the heat flux at a particular pressure and ΔT was dependent upon the population of active sites. They observed[8,9] that the number of active sites always increased as ΔT increased and concluded that drop coalescence plays an active role in dropwise condensation because new drops can nucleate only on active sites exposed to the vapor.

The latest theory of dropwise condensation was offered by LeFevre and Rose[10] in 1966. They considered heat transfer arising from condensation on a single drop and, by means of an assumed distribution of drop sizes, deduced the mean heat transfer rate for the whole surface. The three principal physical phenomena considered in the evaluation of the heat transfer through a single drop were: the effect of surface tension on the relations between the temperature and saturation pressures for either side of a curved interface, conduction through the drop, and dissipation associated with matter transfer by condensation.

Thus, it appears that while advances have been made, the mechanism of dropwise condensation is far from being clearly understood.

LITERATURE SURVEY

Criteria for Dropwise Condensation

To analyze factors which determine if the condensation process in a given system will be filmwise or dropwise, it will be necessary to examine the forces acting on a condensed drop. The forces acting upon

a droplet adhering to a surface are represented in Figure 1, where σ_{lv}, σ_{sv}, and σ_{sl} represent the interfacial tensions which are equivalent to the surface molecular forces at the liquid-vapor, solid-vapor, and solid-liquid interfaces. At equilibrium:

$$\Psi = \sigma_{sv} - \sigma_{sl} = \sigma_{lv} \cos\theta \quad . \qquad (5)$$

where Ψ is defined as the Adhesion Tension. θ is the contact angle of the droplet. For $(\sigma_{sv} - \sigma_{sl}) < 0$, $\theta > \pi/2$ and the liquid withdraws from the solid surface to form droplets. However, for $(\sigma_{sv} - \sigma_{sl}) > \sigma_{lv}$, Equation (5) cannot be satisfied and there can be no equilibrium thereby causing filmwise condensation. Therefore, the function of a dropwise promoter is to reduce the surface tension of the solid-vapor interface, while not reducing proportionately the solid-liquid and liquid-vapor interfacial tensions.

Dropwise Condensation Using Permanent Coatings

Investigation of the phenomenon of dropwise condensation has shown that it is possible to stimulate and maintain dropwise condensation using promoters applied to the condensing surface either as permanent coatings or as continually or intermittently applied compounds. Ideally, a permanent nonwettable surface would be the best method of producing dropwise condensation. This coating could be applied to the condensing surface at the time of manufacture, and the condenser would continue to yield dropwise condensation during its lifetime. However, the survey has shown that there is no such things as a "permanent coating." Published information on various available permanent-type coatings, their effectiveness in maintaining dropwise condensation, and their contribution to the thermal resistance of the condensing surface are discussed below.

Under a U. S. Navy Contract, Westinghouse[11] investigated the use of permanent, nonwetting agents for the coating of steam condenser tubes. A screening apparatus was set up to check the heat transfer rates and indicate durability of several promoters prior to testing on actual pilot condenser. The promoters investigated in this manner were Dow Corning Silicones DC-1107, R-671, XR-4010, R-875 and R-991, and teflon (polytetrafluoro ethylene). The initial check showed that XR-4010, R-875 and R-991 were completely ineffective. The performance of other coatings is shown in Figure 2. The observed improvement in overall coefficient of heat transfer over the uncoated plate was approximately 50% for DC-1107, 20% for teflon, and 15% for R-671. An examination of the duration of effectiveness of these coatings on flat copper plates showed that teflon was the only coating of sufficient life expectancy (over 125 hours) to warrant further investigation.

The heat exchanger tubes in the final test were 90-10 copper nickel arranged horizontally in 4 rows and 9 columns, and separated by a vertical baffle in between the second and third row. The 18 tubes on one side of the baffle were coated with 0.5 mil thick teflon and the 18 tubes on the other side of the baffle were uncoated to facilitate comparison. The results are shown in Figure 3.

After approximately 40 hours of experimentation, dropwise condensation was observed on the uncoated tubes also which was ascribed to surface contamination by oil carried over with the steam. The results for the oil contaminated tube are also plotted in Figure 3 for comparison. It may be seen that the overall coefficient of heat transfer improved by 22% and 50% respectively for the teflon coated and the contaminated tubes over the uncoated tubes.

Some experimental work has been carried out at the U. S. Naval Ship Research and Development Center, Annapolis, Maryland, to determine the effectiveness and durability of teflon over a period of time. For this purpose, a small 3-pass, 74-tube, air-ejector after-condenser was modified to serve as a test condenser for the teflon coated tubes. The tubes were 5/8-inch O.D., No. 185WC of 90-10 copper-nickel, coated with 0.0005-inch teflon on the outside.[12]

The condenser was operated for a total period of 4534 hours with heat transfer evaluation tests at four intervals; at the start of the test, and after 708, 2652, and 4534 hours. The performance of the teflon coated tube condenser after 4534 hours showed a reduction in the overall heat transfer coefficient of approximately 22% of the value at the start of test. This decrease was attributed to a gradual transition from dropwise to filmwise condensation which increased the heat flow resistance. This apparently occurred due to a thin film of iron oxide that enveloped the tube condensing surface and affected the nonwetting property of the teflon coating. However, evaluation tests conducted after the steam side of the tubes was cleaned showed that some permanent deterioration of the nonwetting property of teflon had occurred. The removal of iron oxide increased the heat transfer coefficient, but did not restore them to the original value obtained at the beginning of the tests. The results of these tests are tabulated in Table 1.

Topper and Baer[13] introduced the concept of using teflon on tubular surfaces to obtain dropwise condensation as early as 1955. They showed considerable improvement in the overall coefficient of heat transfer. Later, Swortzel[14] used teflon to induce dropwise condensation of steam on a vertical condensing tube. The condensation was carried out at atmospheric pressure on a 35-inch long, 1/2-inch I.D. copper tube. The method of application of teflon consisted of first lightly sandblasting the tube to assure a clean surface followed by spraying the tube with one coat of teflon and fusing it in an electric oven at 700°F. The thickness of the teflon film was found to be less than 0.001 inch. He

found the condensing steam film coefficients to be from 240 to 330 percent over those of the copper tube before it was coated with the teflon promoter.

Depew and Reisbig[15] conducted an experimental program to study the behavior of a 0.00025-inch thick film of teflon to promote dropwise condensation on a 1/2-inch O.D. aluminum tube. The tube was mounted horizontally and both the dropwise and filmwise condensations were studied. They found that curves of heat transfer coefficients versus vapor to surface temperature drop in dropwise and filmwise condensation converged as the temperature drop became large. This was caused by the rapid formation of drops which tend to blanket the condenser surface with liquid at high heat fluxes. The authors also found that highest heat transfer coefficients were obtained with thinnest teflon films because of the high thermal resistance of teflon. A teflon film thickness of 0.00025-inch provided 12.5 times as much thermal resistance as the 0.02-inch thick aluminum wall of the condenser tube and about 3 times more than the condensing film itself. This shows that the thickness of the teflon film is an important parameter and it should be kept at a minimum to improve the overall performance of the teflon-coated condenser tubes. It is claimed that teflon films as thin as 0.00005 inch can be produced although the production of such a thin film will be most difficult.

A short experimental program to induce dropwise condensation using teflon was also carried out at the Naval Civil Engineering Laboratory and reported in 1963 by Saturnino.[16] He observed that dropwise condensation gave overall heat transfer coefficients which were 2 to 5 times greater than those corresponding to filmwise condensation. The teflon thickness in these experiments was estimated at 0.001 inch.

Erb and Thelen[17,18] and Erb[19,20] have been conducting a research program in dropwise condensation at the Franklin Institute Research Laboratory using gold, silver, and Parylene-N polymers, as condensation promoters. Erb[19] reported that a 0.127μ thick coating of gold on 127μ thick silver on 127μ thick nickel on 90-10 copper-nickel tubes produced dropwise condensation even after 3650 hours of continuous operation with steam at 101°F. An improvement in the overall coefficient of heat transfer of 50% was obtained. The estimated cost of this coating was $1.02 per sq ft of the tube surface. Erb and Thelen[17] have reported that a coating of silver on 316 stainless steel tubes provided good dropwise condensation from distilled water as well as seawater. A coating of silver sulphide on mild steel tubes was also claimed to provide dropwise condensation for over 7500 hours of continuous operation. The use of Parylene-N polymers in promoting dropwise condensation was also demonstrated by Erb and Thelen.[18] They formed a 0.25μ thick film of Parylene-N polymer coating on chrome-plated 90-10 copper-nickel tubes and obtained dropwise condensation for over 2600 hours of continuous operation. Using steam at 114°C, an increase in the overall coefficient of heat transfer of 38% was obtained.

Table 1. Results of Heat Transfer Evaluation on Teflon Coated Tube Condenser (Reference 12).

Run No.	Shell Pressure in. Hg Absolute	Condensate Flowrate (lb/hr)	U (Btu/hr ft^2 ^{o}F)	Time in Service (hr)	Reduction in U since the start of test (%)
1	7.12	783	899	0	---
2	6.89	745	827	708	8%
3	7.19	690	739	2652	18%
4	6.98	644	699	4534	22%
5	7.12	720	788	steam side cleaned	12%

Recently, Erb[20] has been successful in maintaining dropwise condensation continuously for over a year on 90-10 copper-nickel which had a 5μ thick bright silver deposit followed by a 0.025μ thick electrodeposited gold. Compared to the unplated tube, the heat transfer efficiency was found to be increased by up to 100%. Also, he has observed a 40% increase in the overall coefficient of heat transfer after 2 years of continuous condensation using 1μ thick deposit of Parylene-N on chromium plated 90-10 copper-nickel. Additional studies are now being conducted on coatings based on gold, silver, Parylene-N polymers, teflon, and other fluoro-carbon resins.

Dropwise Condensation Using Organic Promoters

No condenser tube material having the combination of thermal, mechanical and chemical properties required for sustained dropwise condensation has yet been found. Therefore, the condenser surface properties must be altered with the application of a thin layer of some substance having a low affinity for the vapor and a very high affinity for the metal.

Investigators have been testing a wide variety of organic compounds to produce dropwise condensation. Any compound which consists of a relatively active radical would be suitable for this purpose if the molecules were oriented with the active part adsorbed on the cooling surface, and the inactive part acting as a surface upon which the vapor molecules can condense. In such an arrangement, the active promoter needs to be only one molecular layer thick. In computing the amount of promoter required to form one molecular thick layer, allowance should be made for the relatively rough surface finish of commercially available condensing surfaces which will result in a corresponding increase in the active surface area.

Drew, Nagle and Smith[21] conducted one of the earliest series of tests to determine the effectiveness of various organic compounds in promoting dropwise condensation. Their findings are detailed in Table 2. Only those compounds which caused dropwise condensation to be maintained for at least 24 hours without promoter renewal are listed in the Table. Most of these tests were carried out with steam condensing at atmospheric pressure. They concluded that:

- mineral oils are ineffective as promoters for condensation on metal surfaces
- higher molecular weight fatty acids are very effective promoters for all metals
- alcohols, organic nitrogen compounds, and halides are ineffective as promoters

- only those substances which are strongly absorbed or otherwise firmly held to the condensing surface are significant dropwise promoters

Nagle et al[22] conducted tests on a 2-1/2-inch I.D. x 2-7/8-inch O.D. x 24-inch long vertically mounted copper pipe. Dropwise condensation of steam was carried out on the outer surface of this tube at 5 psig using oleic acid as the dropwise promoter. They obtained overall heat transfer coefficients which were 50% to 350% greater than those in filmwise condensation under identical operating conditions, with an average improvement of about 80%.

Fatica and Katz[23] carried out measurements of heat transfer, contact angle, and number of drops per unit area on a 3-inch x 1-inch copper plate mounted vertically. The dropwise condensation was promoted by stearic and oleic acids on copper, chromed copper, and nickel plated copper surfaces. They observed a substantial increase in the overall coefficient of heat transfer compared to that obtained in filmwise condensation. The experience of Hampson[24] in Britain, however, has shown that the use of oleic acid as a promoter was not always successful whereas the use of benzyl mercaptan was always successful on copper or brass surfaces. Hampson[25] also found xanthates, dithiophosphates, synthetic resins such as bakelite and the silicones to be effective in maintaining dropwise condensation. He also noted that an excess of promoter on the surface, which resulted from its injections into the steam, caused a considerable reduction in the heat transfer rate in dropwise condensation. His work included investigation of the effects of surface finish on dropwise condensation which will be dealt later in this survey.

Filming amines, e.g., $C_{13}H_{27}NH_2$, have been shown by Tanzola and Wiedman[26] to induce dropwise condensation on metal surfaces thereby increasing the overall coefficient of heat transfer by a factor of three when used in full scale steam plants. This increase is very substantial in view of the fact that the overall coefficient of heat transfer is controlled by a number of thermal resistances only one of which is controlled by the condensation mode. This may be illustrated by an example. Consider a practical condenser as represented in Figure 4. The overall coefficient of heat transfer may then be written:

$$\frac{1}{U} = \frac{t}{K} + \frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3} \qquad (6)$$

where K = thermal conductivity of metal wall of the condenser, Btu/hr ft °F

t = thickness of the metal wall of condenser, ft

h_1, h_2 and h_3 = coefficients of heat transfer as shown in Figure 4

Table 2. Promoters which Maintained Dropwise Condensation for at Least 24 Hours (Reference 21).

Group	Promoter	Condensing Surface
Fatty Acids	Shearic acid $C_{17}H_{35}COOH$	Copper, Brass, Chrome-Nickel Steel
	Oleic acid $C_{17}H_{33}COOH$	Copper, Brass, Chrome-Nickel Steel, Nickel, Chromium Plate
	Linoleic acid $C_{17}H_{31}COOH$	Monel
Fats & Waxes	Beeswax	Copper, Chrome-Nickel Steel
	Fatty binders in buffing compounds	Copper, Chrome-Nickel Steel
Mercaptans	Benzyl mercaptan $C_6H_5CH_2SH$	Copper, Brass, Monel
Xanthates	Potassium amyl xanthate $C_5H_{11}OCSSK$	Copper, Brass
Dithiophosphates $HSSP(OR)_2$	"Aerofloat 15"	Copper, Brass
	"Aerofloat 25"	Copper, Brass

Assuming the condensing surface to be 1/4-inch thick cast iron, a conductance of condensing steam of 1000 Btu/hr ft^2 °F, a conductance of heated water of 300 Btu/hr ft^2 °F, and a corrosion film conductance of 150 Btu/hr ft^2 °F, the overall coefficient of heat transfer is given by:

$$U = \frac{1}{\frac{0.25}{320} + \frac{1}{1000} + \frac{1}{300} + \frac{1}{150}}$$

$$= 85 \text{ Btu/hr ft}^2\ ^\circ\text{F}$$

The use of a promoter generally prevents corrosion of the condensing surface therby eliminating its resistance to heat transfer. It may now be noted that to obtain a 3-fold increase in the overall coefficient, a 20-fold increase in condensing coefficient is necessary. To translate this order of magnitude of improvement in the condensing coefficient to the overall coefficient, it will be necessary to increase the water side conductance and decrease the thermal resistance of the metal wall by similar proportions.

Blackman and coworkers[27] investigated a number of compounds which could be used to promote dropwise condensation. They concluded that active promoters have in the molecule an unhindered hydrocarbon chain which confers water-repellency on the compound and an "anchoring" group which is usually a divalent sulphur atom. This investigation is considered to be the most elaborate study in dropwise promoters to date, and will be discussed in some detail here in order to list the various promoters, their effective lives, and their minimum concentration necessary to cause dropwise condensation.

In all of the tests, the following precautions and method of promoter application to the condensing surfaces were observed. All traces of grease and other possible contaminants were removed from the apparatus. The condensing surface consisted of bright polished metal and the condenser tube was completely wettable with cold water. Successive treatments with emery paper, mild abrasive powder, and a mixture of mild abrasive powder and detergent powder produced the desired condensing surface. The promoter was generally applied to this condensing surface in the form of a solution in a low boiling solvent, e.g., ether, acetane or carbon tetrachloride. A solution strength of about 1% was used.

The compounds listed in Table 3 were found to produce perfect dropwise condensation (i.e., no filmwise condensation) for at least 500 hours, during which time the condensate showed no change in appearance. For some promoters, condensation was terminated for a few days and restarted successfully. Some other promoters were tested for even longer periods of time and found to maintain dropwise condensation over the entire duration of testing with no deterioration. These compounds are

listed in Table 4. Three promoters were tested on brass and copper surfaces to determine minimum promoter concentration necessary to sustain dropwise condensation. The minimum effective concentrations of these promoters are listed in Table 5. The authors concluded that the minimum effective concentration of the compound might depend upon any one or more of the following factors: (a) actual concentration of the compound, (b) the molecular concentration of the compound, (c) the molecular concentration of sulphur, and (d) the molecular concentration of the active hydrocarbon radical.

Table 6 lists a total of 13 compounds which promoted perfect dropwise condensation but were tested for only 2 hours. Four other compounds tested were found to be either poor or completely ineffective dropwise condensation promoters. The ineffectiveness of sodium dodecylsulphonate ($C_{12}H_{25}SO_3 \cdot Na$) led the authors to believe that a sulphur atom having all of its valence electrons in use cannot form a bond with the metal surface. This conclusion was confirmed by testing dioctadecyl sulphoxide $[(C_{18}H_{37})_2SO]$ and sulphane $[(C_{18}H_{37})_2SO_2]$ for effectiveness as dropwise condensation promoters. The former, which has two unused valence electrons, was found to be an effective dropwise promoter whereas the latter, which has no unused valence electrons, did not promote dropwise condensation.

The authors concluded that compound which, when oriented at the metal surface in a monolayer, presented an "unhindered" hydrocarbon surface to the steam, were successful in promoting dropwise condensation. The surface-active groups contained divalent sulphur or selenium. No correlation between the structure of the compound and their effective life was obtained.

Furman and Hampson[28] have also reported an experimental investigation in filmwise and dropwise condensation of steam. A strong solution of dioctadecyl xanthate, $C_{18}H_{37} \cdot O \cdot C \cdot S \cdot S \cdot C_{18}H_{37}$, in carbon tetrachloride was applied to the condensing surface to promote dropwise condensation which improved the overall coefficients of heat transfer by a factor of between 2 and 3. Welch and Westwater[4] found cupric oleate an excellent promoter on copper, stainless steel, inconel and copper-nickel surfaces. The promoter was found to be ineffective on aluminum and monel. With this promoter using a copper surface, perfect dropwise condensation occurred with ethylene glycol and glycerine.

Bobco and Gosman[29] used fluorochemicals as dropwise promoters. Perfluorinated acids were found to produce dropwise condensation of pure vapors of iso-octane, iso-heptane, cyclo-hexane, carbon disulphide, and decalin. The use of these compounds in practical condensers is, however, questionable due to their corrosive action on the condensing surface and their short useful life as condensation promoters.

Table 3. Compounds Producing Perfect Dropwise Condensation for at least 500 Hours (Reference 27).

$KS \cdot SC \cdot O \cdot (CH_2)_{10} \cdot O \cdot CS \cdot SK$	OO-decamethylene di(potassium xanthate)
$C_2H_5S \cdot SC \cdot O \cdot (CH_2)_{10} \cdot O \cdot CS \cdot SC_2H_5$	OO-decamethylene di(ethyl xanthate)
$C_{12}H_{25}S \cdot CS \cdot SC_{12}H_{25}$	Didodecyl trithiocarbonate
$C_{12}H_{25}S \cdot CO \cdot (CH_2)_8 \cdot CO \cdot SC_{12}H_{25}$	Didodecyl decane-1: 10-dithionate
$C_{12}H_{25}S \cdot CO \cdot (CH_2)_{10} \cdot SeCN$	Dodecyl 11-selenocyanatoundecanethiolate
$C_{18}H_{37} \cdot SCN$	Octadecyl thiocyanate
$C_{18}H_{37} \cdot Se\ CN$	Octadecyl selenocyanate
$CH_3 \cdot CO \cdot NH \cdot CS \cdot SC_{18}H_{37}$	Octadecyl N-acetyldithio-carbamate
$C_{18}H_{37}S \cdot CO \cdot NH_2$	Octadecyl thiolcarbamate
$C_{18}H_{37} \cdot SH$	Octadecanethiol(stearyl mercaptan)
$C_{12}H_{25}S \cdot (CH_2)_{10} \cdot SC_{12}H_{25}$	1:10-Bisdodecyl thiodecane
$(C_{12}H_{25}S)_4\ Si$	Tetrakis (Decylthio)silane
$(C_{12}H_{25}S)_3\ P$	Tri(dodecylthio)phosphine
$(C_{12}H_{25}S)_4\ P_2S_3$	Di(bisdodecylthiophosphinothioyl)sulphide
$(C_{18}H_{37}O)_2\ PS \cdot SH$	OO-dioctadecyl hydrogen phosphorothiolothionate
$(C_{18}H_{37}O)_4\ P_2S_3$	Di(bis-stearyloxyphosphinothioyl sulphide)

Table 4. Compounds Promoting Dropwise Condensation for Very Long Period of Time (Reference 27).

Compound	Dropwise Condensation for at least
$C_6H_5 \cdot CH_2 \cdot S \cdot CH_2 \cdot C_6H_5$	1730 hours
$C_{18}H_{37} \cdot O \cdot CS \cdot SC_2H_5$	1350 hours
$C_{18}H_{37} \cdot O \cdot CS \cdot S \cdot (CH_2)_{10} \cdot S \cdot CS \cdot OC_{18}H_{37}$	1680 hours
$CH_2 \cdot O \cdot CO \cdot (CH_2)_{10} \cdot S \cdot CS \cdot OC_2H_5$ | $CH \cdot O \cdot CO \cdot (CH_2)_{10} \cdot S \cdot CS \cdot O \cdot C_2H_5$ | $CH_2 \cdot O \cdot CO \cdot (CH_2)_{10} \cdot S \cdot CS \cdot O \cdot C_2H_5$	3530 hours
$C_{12}H_{25}\ Si(SC_2H_5)_3$	1850 hours

Table 5. Minimum Effective Concentration of Promoter for Dropwise Condensation (Reference 27).

Promoter	Brass Surface	Copper Surface
Dodecane thiol $C_{12}H_{25}SH$	0.12%	0.03%
Dodecyltrisethylthiosylane $C_{12}H_{25} \cdot Si(SC_2H_5)_3$	0.25%	0.125%
Dodecyl octadecanethiolate $C_{17}H_{35}CO \cdot S \cdot C_{12}H_{25}$	0.25%	0.25%

Table 6. Compounds that Promoted Perfect Dropwise Condensation (tested only for 2 hours, reference 27).

1. $C_{18}H_{37}O{\cdot}CS{\cdot}S{\cdot}(CH_2)_{10}{\cdot}COOH$
2. $C_{18}H_{37}S{\cdot}CS{\cdot}O{\cdot}(CH_2)_{10}{\cdot}O{\cdot}CS{\cdot}SC_{18}H_{37}$
3. $C_{18}H_{37}CO{\cdot}SC_{12}H_{25}$
4. $C_{12}H_{25}{\cdot}S{\cdot}CO{\cdot}(CH_2)_{10}{\cdot}SCN$
5. $CH_3{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}S{\cdot}(CH_2)_{10}{\cdot}CO{\cdot}SC_{12}H_{25}$
6. $HS{\cdot}(CH_2)_{10}{\cdot}CO{\cdot}S{\cdot}(CH_2)_{10}{\cdot}S{\cdot}CO(CH_2)_{10}{\cdot}SH$
7. $CH_3{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}S{\cdot}(CH_2)_{10}{\cdot}CO{\cdot}S{\cdot}(CH_2)_{10}{\cdot}S{\cdot}CO{\cdot}(CH_2)_{10}{\cdot}S{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}CH_3$
8. $Se{\cdot}CN{\cdot}(CH_2)_{10}{\cdot}Se{\cdot}CN$
9. $NH_2{\cdot}CO{\cdot}S{\cdot}(CH_2)_{10}{\cdot}S{\cdot}CO{\cdot}NH_2$
10. $C_{12}H_{25}{\cdot}SH$
11. $C_{18}H_{37}{\cdot}S{\cdot}C{\cdot}(NH_2)_2{\cdot}O{\cdot}C_6H_2(NO_2)_3$
12. $C_{18}H_{37}{\cdot}S{\cdot}C_{12}H_{25}$
13. $C_6H_5{\cdot}SH$

Watson and coworkers[30] suggested the use of waxes derived from plants as promoters. They recommended the use of lotus-leaf wax, Irish peat wax and montan wax. These waxes consist of esters, acids and alcohols of hydrocarbons with chain lengths of between 20 and 30 carbon atoms, and are comparable with the filming amines and sulphur-linked hydrocarbons having -OH and -COOH "anchors" in place of the $-NH_2$ and -SH anchors but with considerably longer hydrocarbon chains. They found that to maintain highest value of the overall heat transfer coefficients on a copper tube, it was necessary to inject the promoter at the rate of 0.1 gm per sq ft of the condenser surface at intervals of 200 hours. The time interval had to be reduced to 100 hours for successful dropwise condensation on aluminum, brass and cupro-nickel condensing surfaces.

Osment and coworkers[31] performed a series of life tests on nine organic promoters and four different metals using industrial steam. The four metals were 70-30 brass, 2% aluminum brass, 70-30 cupro-nickel and monel. The steam was obtained directly from the plant boiler and supplied to the condensers at about atmospheric pressure. The condenser tubes were promoted by complete immersion in a solution of the promoter for 15 minutes. The treated tubes were exposed to air for 2, 6, or 24 hours before being fitted into the condenser. Each combination of metal, promoter, and air exposure was tested four times. The promoters tested are listed in Table 7.

The effective lives of the promoters were found to be inconsistent and, generally, comparatively short, the average life varying between 50 and 300 hours; except for Monel, for which all promoters gave very short lives. The general nature of the breakdown strongly suggested that failure was caused predominantly by fouling.

The testing was extended to include drop promotion by promoter injection into the steam at regular intervals. Using 100 cc of 1% solution of promoter No. 9 of Table 7 in carbon tetrachloride, perfect dropwise condensation on all four types of tubes was obtained which lasted for 100 hours. Dropwise condensation was maintained continuously when the promoter was injected every 100 hours of operation. However, a 2% solution of the same compound in paraffin maintained perfect dropwise condensation for a year of continuous operation when the con entration of the promoter used was 0.05 ppm of the steam condensed. Similarly, a 1% solution of compound No. 5 of Table 7 produced perfect dropwise condensation on all 4 metal surfaces and maintained it for a year of continuous operation when the promoter was injected at regular weekly intervals. The amount of promoter used was 0.01 ppm of the steam condensed.

Table 7. Dropwise Condensation Promoters
(reference 31)

No.	Name	Formula
1	Dioctadecyl diselenide	$C_{18}H_{37}SeSeC_{18}H_{37}$
2	Dioctadecyl xanthate	$C_{18}H_{37}$-O-C-S-S-$C_{18}H_{37}$
3	Didodecyl trithiocarbonate	$C_{12}H_{25}$S-C-S-S-$C_{12}H_{25}$
4	Dioctadecyl disulphide	$C_{18}H_{37}$-S-S-$C_{18}H_{37}$
5	Tetrakis(dodecanethio)silane	$Si(S\ C_{12}H_{25})_4$
6	Dodecanetris(ethane thio)silane	$C_{12}H_{25}Si(S\text{-}C_2H_5)_3$
7	OSS-tri-octadecane phosphorodithioate	$(C_{18}H_{37}O)_2PSSC_{18}H_{37}$
8	Octadecyl seleocyanate	$C_{18}H_{37}SeCN$
9	Montan wax	

These experiments suggest that frequent cleaning of tubes to remove grease, scale, etc., may not be necessary for continuous dropwise condensation. However, the overall coefficient of heat transfer was found to decrease with time, as shown in Figure 5 for brass and cupro-nickel tubes using tetrakis(dodecanethio)silane as the promoter. Thus, it appears that although injection of a promoter at regular intervals may be sufficient to promote and maintain dropwise condensation for continuous operation, the condenser surface will have to be frequently degreased or cleaned to ensure the benefits of dropwise condensation in providing high overall heat transfer rates.

Hampson[1] conducted a study to determine the durability of various promoters in maintaining dropwise condensation. He concluded that mixed promoters maintained dropwise condensation for longer periods of time than single promoters, and different promoters have differing effectiveness on various metals.

Brunt and Minken[32] conducted an investigation into the effect of dropwise promoters on the operations of commercial seawater evaporators and showed improvements in the overall coefficient of heat transfer. They concluded that a reduction of 30 percent in the capital cost of seawater evaporators could be achieved using dropwise condensation promoters recommended in reference 27. To estimate the effectiveness of dropwise condensation promoters in commercial condensers, Butcher and coworkers[33] conducted tests on the condenser of a 350 kw turbo-alternator set. They used solutions of mixtures of straight-chain fatty acids of high molecular weight in liquid paraffin as dropwise condensation promoters by injecting them into the turbine exhaust steam to give a total coverage in the condenser of about 1 ml/ft^2 of the heat transfer surface. They observed that improvement in condenser performance was less marked than that obtained in small laboratory rigs. The improvement in the overall coefficient of heat transfer was about 20%. It was suggested that improvement in the condenser performance was limited by the water side coefficient and the metal wall resistance.

Birt and coworkers[34] have also investigated the use of promoters in seawater evaporators. Their full scale test program showed that improvements in overall heat transfer coefficients of about 30% can be achieved by using dropwise promoters. They concluded that injection of dropwise promoters into steam is a valuable technique for maintaining high heat fluxes.

Bliss and Harding[35] used lard oil to promote dropwise condensation. Similar to the observations of Butcher,[33] they also reported that improvements in heat transfer on the condensation side has little effect upon the overall coefficient of heat transfer due to the metal wall resistance and the coefficient of heat transfer in evaporation on the other side of the condensing surface. They noted substantial improvements in the overall coefficient of heat transfer when brine was maintained under forced circulation on the cooling side of the condensing surface.

Brown and Thomas[36] considered the effects of low absolute pressures on the condensation process. Such pressures are used in the steam turbine condensers. Two 3/4-inch diameter, 42-inches long, admiralty brass tubes were used as condensing tubes and coated on the outside with a layer of approximately 0.0001 inch thick teflon to induce and maintain dropwise condensation. They found the overall coefficient of heat transfer to increase with the absolute pressure for both the dropwise and the filmwise condensations. The overall coefficients in dropwise condensation were found to be between 2 to 3 times those for filmwise condensation. The fall-off in the overall coefficient of heat transfer with falling pressures was more marked for dropwise condensation than for filmwise condensation.

Sugawara and Katsuta[37] used dimenthylpolysiloxane, $[(CH_3)_2\ SiO]_n$, as a promoter on a copper condensing surface and observed the condensation process microscopically. The copper plate was 17 cm x 4 cm x 0.3 cm thick. Their observation confirmed the estimates by Welch and Westwater[5] of the critical thickness of the condensate film to be between 0.4 and 0.7 micron (observed to be 0.63 micron) and the critical nuclei diameter calculated from Fatica and Katz[23] equation, 8.8 micron, agreed well with the calculated value of 8.7 micron by McCormick and Baer.[38]

Dolloff and Metzger[39] recently completed a study of dropwise condensation of steam at high pressures. They used cupric oleate at a concentration of 72 ppm as a promoter. They observed that the heat transfer coefficient had its maximum value at low ΔT and decreased to an essentially constant value depending on pressure at high ΔT. Similar to the observation of Brown and Thomas,[36] they observed an increase in the coefficient of heat transfer with an increase in pressure at which condensation took place.

Increased Heat Transfer Rate by Mechanical Wiping

Two reports were published in 1967 which showed advantages of periodic mechanical removal of steam condensate from a condensing surface. The concept is analogous to the ordinary automobile windshield wiper where, with proper blade design, the liquid film may be almost completely removed. The wiping action of the blades provides a fresh condensing surface periodically. Bauman[40] conducted a study on a 18 inch diameter x 6 inch high cylinder which was wiped on both the inner and outer surfaces with automobile type wiper blades. He obtained overall coefficients of heat transfer which increased with the wiper speed, and with the coolant velocity. An increase in the overall coefficient of heat transfer of 60% was obtained at a wiper speed of 180 rpm compared to its value without wipers. Adamson[41] extended the work of Bauman to shipboard application of the principle. He has suggested the use of wipers in condensers operating at various load cycles. The wiper blades would

then be engaged during peak or near-peak load conditions only. The report details several designs of wiper blades for shipboard application.

Effect of Condenser Surface

As early as 1935, Drew, Nagle and Smith[21] reported the effect of surface finish on dropwise condensation. Their experiments showed that very smooth, or polished surfaces induced dropwise condensation, even in the absence of oil or fatty acids. On the other hand, they concluded that film condensation can occur on very rough or very foul surfaces even if coated with oil or fatty acids. It therefore appears that in the absence of additives or promoters, it is necessary to have a smooth surface to induce dropwise condensation.

Hampson[25] noted that a mirror polish increased the life of a brass surface promoted with oleic acid to 4 times for finishes with numbers 3-0000 grades of emery paper. He also noted that very clean and smooth surface actually caused filmwise condensation at first which later changed to dropwise condensation due to impurities in the steam.

The basic mechanism of promotion and maintenance of dropwise condensation lies in the fact that the condenser surface should be nonwettable to the condensing vapor. Any surface treatment, including application of dropwise promoters, which will cause the surface to become nonwettable will be effective in promoting dropwise condensation. Therefore, it becomes apparent that the nature of the metal surface and material determines to some extent if a given promoter will be successful in promoting dropwise condensation. Hampson[1] has confirmed this in his experiments in which he showed that the use of different promoters on the same metal surface caused dropwise condensation for different durations in time. He noted that using a mixture of oleic acid and light lubricating oil as a promoter on the surfaces of mirror smooth chrome-plated copper and No. 0 emery paper treated stainless steel, the useful promoter life for chrome-plated copper was twice as long as for stainless steel. He also found that a promoter of some sort was necessary for dropwise condensation and that highly polished surface alone will not cause dropwise condensation. His observation appears to be contrary to those of Drew, Nagle and Smith.[21] However, this difference may well be caused by degree of surface polish and cleanliness observed during tests.

Misra and Bonilla[42] observed in their experiments with condensing mercury vapor on different surface that it condensed in a dropwise manner on carbon steel and stainless steel surfaces, and in a filmwise manner on nickel and copper surfaces. They noted with the stainless steel condensing surface that even extreme care in cleaning the surface did not produce filmwise condensation.

An elaborate study of surface characteristics to determine the nucleation sites for dropwise condensation has been reported by McCormick and Westwater.[7] The nucleation of water drops during dropwise condensation

was studied on a horizontal surface of copper coated with a monolayer of benzyl mercaptan. Photographic evidence showed that drops nucleated at natural cavities on the condenser surface. Some cavities were nucleation sites because they contained trapped, liquid water. In addition, the authors found that the cavities produced by needles and by spark erosion and scratches made on the surface also nucleated drops. These experiments were extended to include the effect of small solid particles on the condenser surface.

The authors studied the behavior of 37 possible sites in the photographic study. Out of this total of 37 sites, six were found to nucleate from 2 to 5 times after which these sites became inactive. In a total of 8 runs, they found six sites which did not nucleate at all, and 4 sites which nucleated in 7 runs. Drops also appeared from other locations on the surface which could not be identified as nucleation sites from photographs of the surface. They concluded that drops nucleate at preferred sites during dropwise condensation.

To study the effect of small particles on the condenser surface, particles of 24 different materials were tested for effectiveness as nucleation centers. The particle density in these tests varied between 800 and 55,000 particles per square centimeter. They found that the nucleation characteristics of a particle was independent of the particle density whereas nucleation ability among various kinds of particles varied substantially. The relative order of nucleating abilities of these particles was explained by the net heat of adsorption. A positive net heat of adsorption of the vapor on the solid was assumed to mean a spontaneous process. Nucleation of drops was found to occur on particles of 13 materials having positive net heats of adsorption. For the insoluble, wettable particles, a size range of active nucleation sites of about 2μ - 30μ was observed.

McCormick and Westwater showed in a later paper[8] that at a particular pressure and temperature difference, the heat flux increases with an increase in the population of active sites on the surface. However, as the population of active sites increases, the crowding effect reduces the growth rate for each new drop added to the total. It was estimated that when an active site density of between 3×10^6 t 3×10^7 per sq in is reached, the coefficient of heat transfer in dropwise condensation reduces to an extent that it equals the value for filmwise condensation, thereby eliminating the improvements normally expected in dropwise condensation. In addition, the authors observed that the number of active sites depends on the surface preparations and its subcooling. This behavior of sites in condensation seems analogous to their behavior in nucleate boiling.

COMMERCIAL APPLICATIONS OF DROPWISE CONDENSATION

Full Scale Tests

Most of the published work in filmwise or dropwise condensation has been limited to single tube or plate condensers under idealized laboratory conditions. However, a few reports have been published which detail tests conducted on full scale commercial condensers.

Tests using octadecylamine, $C_{18}H_{37}NH_2$, as a dropwise condensation promoter on a full scale steam plant have been reported by Tanzola and Weidman.[26] As discussed earlier, an increase of between 100 to 200 percent in the overall coefficient of heat transfer was obtained. In the drying machine of the paper mill where these tests were conducted, an average reduction of 10 percent in steam requirements was secured through the application of octadecylamine. The authors also noted a sharp reduction in corrosion of the condenser tubes.

Blackman, Dewar and Hampson[27] conducted tests of three drop-promoting compounds on a marine condenser. The three compounds, dodecanethiol, $C_{12}H_{25}SH$, tridodecyl phosphorothioite, $(C_{12}H_{15}S)_3PS$, and decamethylene di(ethylxanthate), $C_2H_5O{\cdot}CS{\cdot}S{\cdot}(CH_2)_{10}{\cdot}S{\cdot}SC{\cdot}OC_2H_5$, were applied on the top surface of about 30 tubes in the condenser. The tubes exhibited dropwise condensation for over 2 years of operation.

Watson, Brunt and Birt[40] postulated the requirements for a material to be used as a drop-promoter in a full scale steam plant as follows:

- both the material and any carrier should be compatible with the steam plant,
- it should be inexpensive and nontoxic,
- it should not require specially cleaned surfaces, and should maintain a clean condensing surface during use,
- it should have a long useful life, and
- it should produce a substantial increase in the steam-side heat transfer coefficient in a reasonable time.

Based upon these requirements, they rejected the usefulness of simple hydrocarbons, fatty acids, sulphur containing hydrocarbons which are injected in solvents such as carbon tetrochloride, and filming amines. They concluded that waxes derived from plants are the best available dropwise condensation promoters, details of which have been given earlier.

A series of life tests were reported by Osment et al[31] using industrial steam condensing in a power generating plant and in a marine condenser, as discussed earlier. Brunt and Minken[32] and Birt et al[34]

have reported a reduction of about 30% in the capital cost of seawater evaporators if dropwise condensation promoters were used whereas Butcher et al[33] reported an increase of about 20% in the overall coefficient of heat transfer. In short, savings of up to 30% could be obtained in commercial condensers with the proper application of the existing knowledge of dropwise condensation promoters.

Effect of Corrosion Inhibitors

Corrosion films on metal surfaces in condensation are usually formed by oxidation of a thin layer of the metal surface. These metal oxides generally have low thermal conductivity thereby offering a significant resistance to heat transfer. The net result is that even if condensing coefficients are increased by an order of magnitude, the net increase in the overall coefficient of heat transfer is very small. If the metal surface could be protected from oxidation, a substantial portion of the increase in condensation coefficient due to drop formation could be translated into an increase in the overall coefficient of heat transfer.

Some organic dropwise condensation promoters have been found to be corrosion inhibitors as well. Filming amines afford corrosion control by the formation of a nonwettable film over the condenser surface. Since these amines do not function by neutralization of carbonic acid, their performances are independent of dissolved gas concentration.

The commonly employed corrosion inhibitors are straight chain primary amines of 10-18 carbon atoms in their molecules, or their salts. Octadecylamines used by Tanzola and Weidman[26] are about the most effective commercially available filming inhibitors. These amines have been known to also lift or loosen and displace existing corrosion deposits on the condenser surface. The usual effective concentration is about 1-3 ppm of the condensate. Since these amines are also dropwise condensation promoters, large increases in the overall coefficients of heat transfer have been obtained with their use. A third, and indirect benefit of corrosion inhibitors is that they increase the condenser life significantly.

Requirements for Practical Use of Dropwise Condensation

For proper application of dropwise condensation to commercial condensers, it will be necessary to carry out life test on full scale condensers under actual operating conditions. To be acceptable, the condenser must be capable of producing dropwise condensation for the life of the equipment and require only a minimum of special handling or servicing. It must yield uniform improvement in heat transfer on a continuous basis and must not cause corrosion by reason of dropwise condensation promoters.

NOT REPRODUCIBLE

Ideally, dropwise condensation will be most successful if the condenser tube material could be inherently capable of producing dropwise condensation, or a permanent coating might be applied at the time of manufacture to promote dropwise condensation with a substantial increase in heat transfer for the life of the equipment without being affected by steam impingement, fouling or deterioration. Neither of these approaches have been successful so far.

At this time, the most suitable method appears to be the intermittent application of the dropwise promoter compound. The compound could be introduced into the condenser either by spraying it onto the tube surfaces periodically or by adding it to the steam source as a fixed predetermined proportion of the condensate.

An area of research which appears promising is the effect of vibration of the condenser surface on coefficients of heat transfer in filmwise and dropwise condensation. Although effects of vibration on coefficients of heat transfer in boiling have been investigated by many authors, no such investigation appears to have been carried out in condensation. It appears feasible that vibration of the heating surface at an appropriate frequency and amplitude may cause break-up of the liquid film in filmwise condensation to form drops, thereby increasing the heat transfer rate. Furthermore, vibration of the condenser surface in dropwise condensation may accelerate drop formation, reduce the drop size necessary for sliding down the condenser surface, and/or increase the sliding velocity of the droplet.

A saving in the capital cost of condensers of around 30%, observed earlier, is substantial and investigation must be continued to realize this saving in seawater evaporators, marine condensers, and other commercial applications. The investigation should also determine if the cost of promoting dropwise condensation is offset by the savings obtained by reduction of the condenser size.

CONCLUSIONS

1. Heat transfer rates in dropwise condensation are significantly higher than those obtained in filmwise or mixed condensation.

2. Condensation on pure, chemically clean metal surfaces is usually filmwise. Very smooth and highly polished surfaces can also cause filmwise condensation. Compounds which make the condenser surface nonwettable are good dropwise condensation promoters when applied to the condenser surface.

NOT REPRODUCIBLE

3. Under laboratory conditions, some permanent-type coatings, e.g., teflon, gold, silver, have been found to be effective dropwise condensation promoters. However, the effective lives of some of these promoters have been short, possibly due to surface fouling or removal of the coating in service. Furthermore, the effectiveness of permanent-type promoters in maintaining dropwise condensation is limited by their low thermal conductivity and the coating thickness.

4. Generally, organic compounds which, when oriented at the metal surface in a monolayer and presented an "unhindered" hydrocarbon surface to the steam, were successful in promoting dropwise condensation. The surface active or anchoring group usually contains a divalent sulphur or selenium atom. A number of such organic compounds have been found which, when applied to the tube surface or fed periodically into the steam stream, are effective dropwise condensation promoters for long periods of time.

5. Only those substances which are strongly adsorbed on the condensing surface are significant dropwise condensation promoters. For example, mineral oils, alcohols, organic nitrogen compounds, and halides are ineffective in promoting dropwise condensation whereas high molecular weight fatty acids and natural waxes derived from plants are good promoters of dropwise condensation.

6. Heat transfer coefficient can be increased by mechanically wiping the condensing surfaces at frequent intervals, the improvement being proportional to the wiping frequency.

7. Corrosion inhibitors which also form a nonwettable layer on the condenser surface are most suitable for achieving dropwise condensation and high overall coefficients of heat transfer.

8. The published information on the durability and behavior of dropwise condensation promoters is incomplete and inconclusive.

9. The applications of condensation promoters are enormous. For example, experiments with commercial seawater evaporators have shown that improvements in the overall coefficient of heat transfer by using dropwise condensation promoters can reduce the capital cost of such equipments by 30% or more. However, due to a lack of needed information on dropwise condensation promoters, they are usually not used in industrial practices.

10. Further research is necessary to determine durability and effectiveness of dropwise promoters under a variety of industrial conditions.

11. It is possible that vibration of the condenser surface may increase heat transfer rates by accelerating drop formation, reducing drop size necessary for sliding down the condenser surface, and/or increasing the sliding velocity of the droplet in dropwise condensation. Vibration of the heating surface in filmwise condensation may cause break up of the liquid film to form drops and increase heat transfer rates.

RECOMMENDATIONS

1. Current research and development programs to increase the useful life of permanent type coatings and organic promoters should and no doubt will be continued. No major breakthrough in the way of new coatings or promoters is in sight. Consequently, the area of greatest potential advancement is in the use of vibrations or wiping techniques. It is, therefore, recommended that an experimental program be initiated to evaluate the effects of vibrating condenser surfaces.

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NOMENCLATURE

A_B	Condenser area free of discrete drops	ft^2
A_T	Total area of the condenser surface	ft^2
h	Film coefficient of heat transfer	Btu/hr ft^2 ^oF
h_1	Coefficient of heat transfer between condensing vapor and the condenser surface	Btu/hr ft^2 ^oF
h_2	Equivalent coefficient of heat transfer across the thin corrosion layer	Btu/hr ft^2 ^oF
h_3	Coefficient of heat transfer between cooling water and the condenser wall	Btu/hr ft^2 ^oF
k	Thermal conductivity of condensate	Btu/hr ft ^oF
K	Thermal conductivity of metal wall	Btu/hr ft ^oF
Q	Rate of heat flow	Btu/hr ft^2
t	Wall thickness	ft
t_c	Critical time for film growth	hr
ΔT	Vapor saturation temperature minus metal surface temperature	^oF
U	Overall coefficient of heat transfer	Btu/hr ft^2 ^oF
X_c	Critical film thickness at fracture	ft
δ	Average film thickness	ft
θ	Angle of contact	^oF
λ	Enthalpy difference between the vapor and the condensed liquid	Btu/lb
ρ	Density of liquid	lb/ft^3
σ	Interfacial tension	lb/ft

σ_{lv}	Liquid to vapor interfacial tension	lb/ft
σ_{sv}	Solid to vapor interfacial tension	lb/ft
σ_{sl}	Solid to liquid interfacial tension	lb/ft
ψ	Adhesion tension	lb/ft

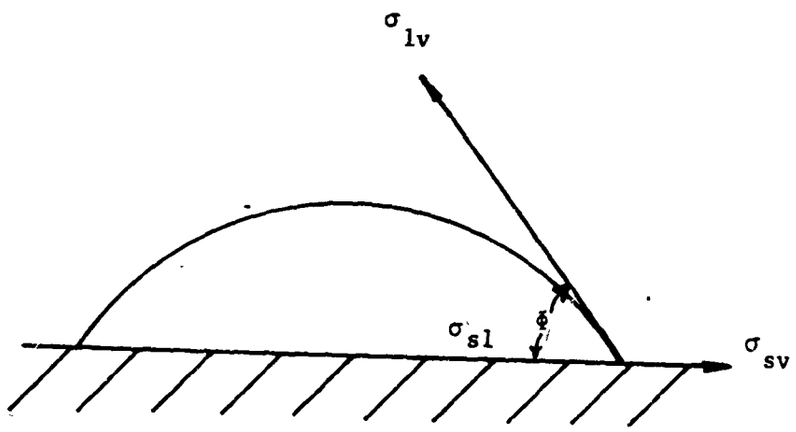

Figure 1. Droplet in contact with a solid.

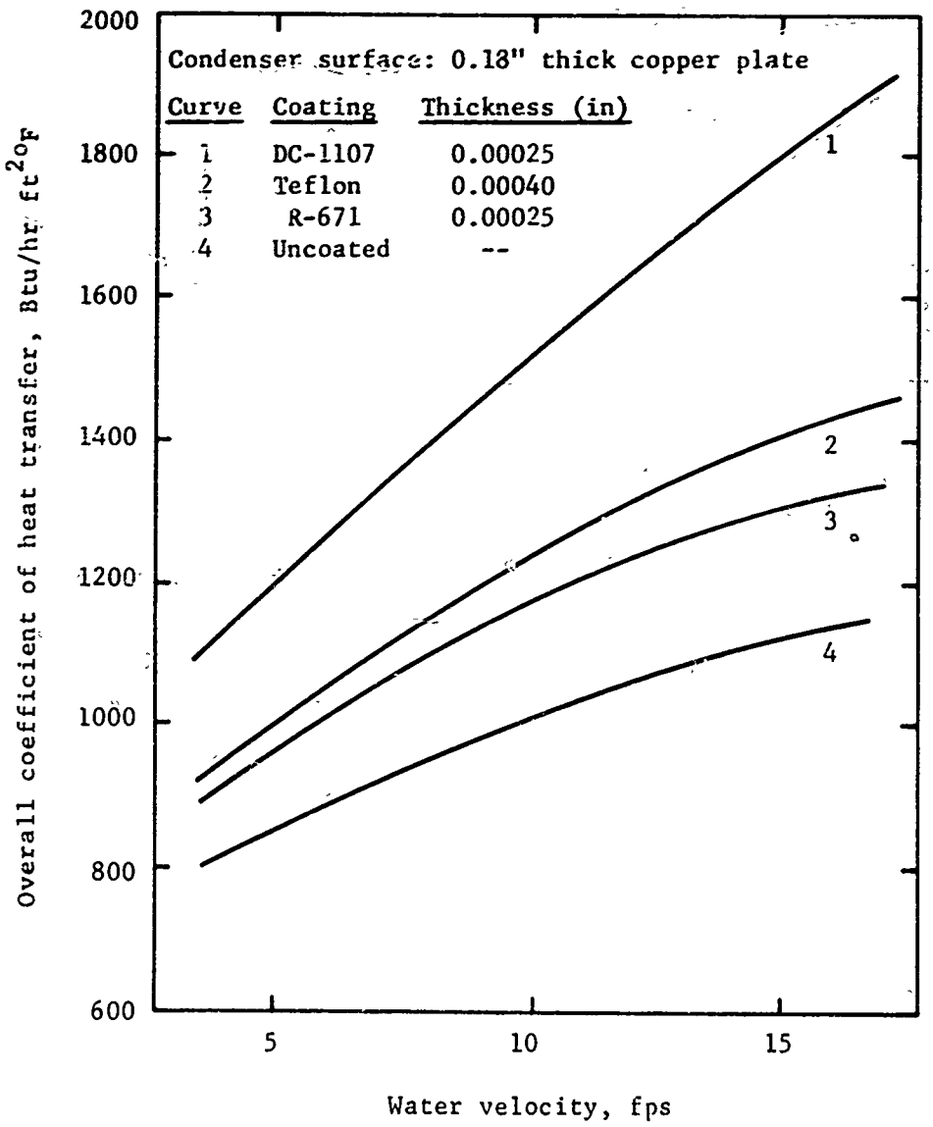

Figure 2. Performance of various coatings in condensation.

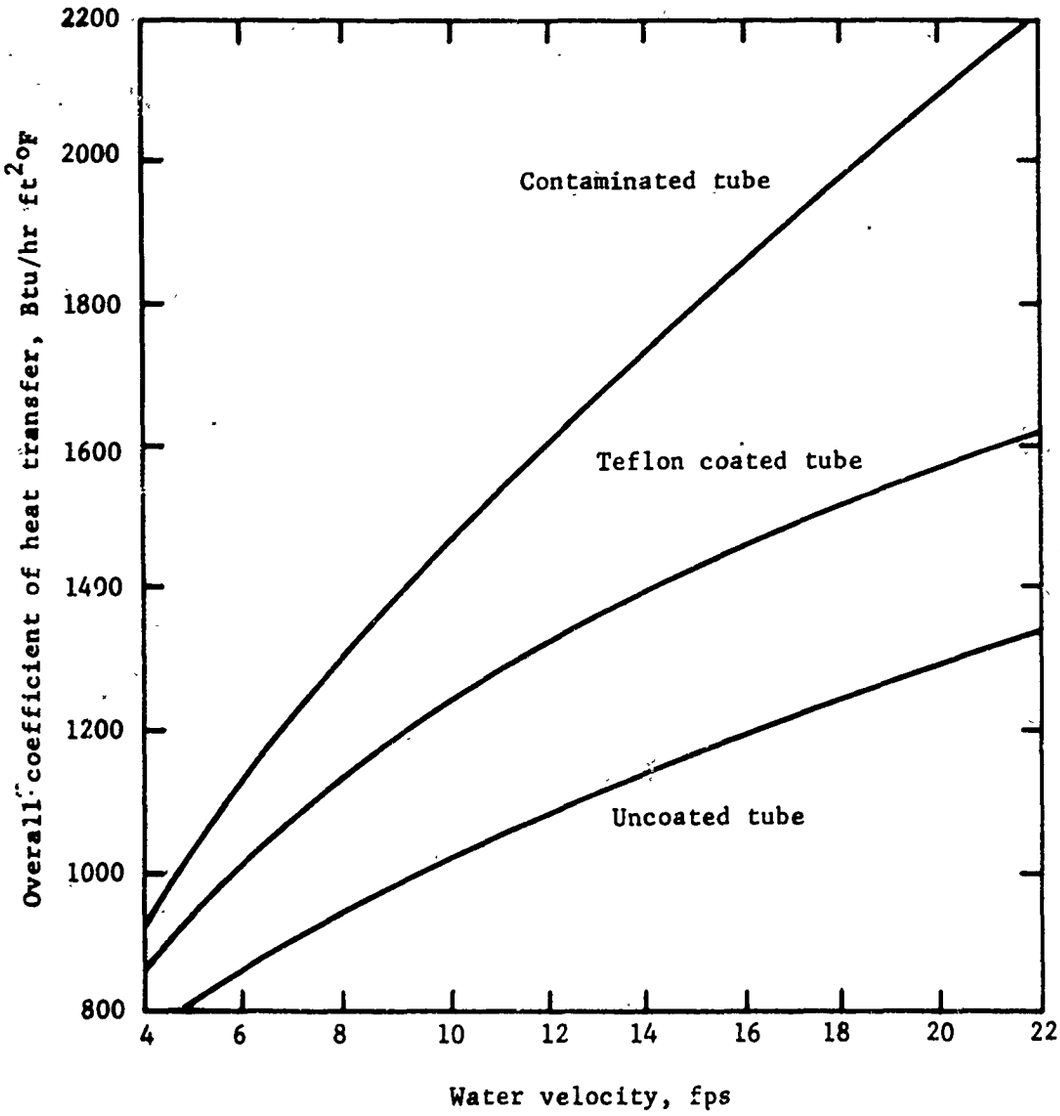

Figure 3. Overall heat transfer rates in condensation with and without teflon coating.

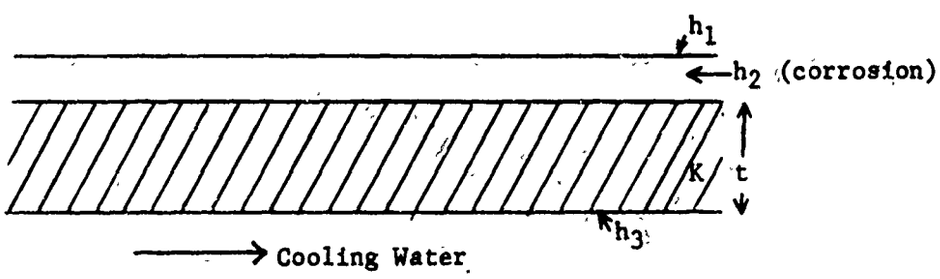

Figure 4. Thermal resistances in a typical condenser system.

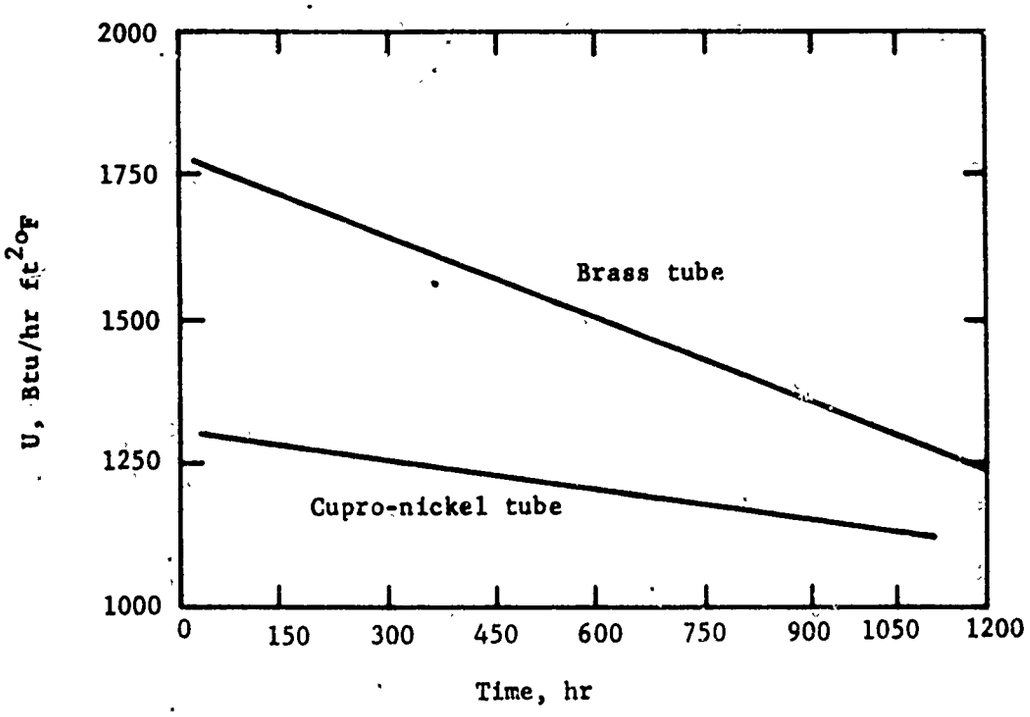

Figure 5. Overall heat transfer coefficient after injection of $Si(SC_{12}H_{25})_4$ in a test condenser.

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13. ABSTRACT

A literature survey of the published information on the effect of coatings and surfaces on dropwise condensation has been carried out. The survey has shown that research to date in promoting dropwise condensation has been limited mostly to small scale laboratory experiments. There appears to be a serious lack of data on methods of application of various dropwise promoters, useful life of promoters, effective concentration, and frequency of promoter renewal. This lack of information is highlighted by the total absence of dropwise condensation as a factor in design of condensers in industry.

Recommendations are made to initiate an experimental program to evaluate the effects of vibrating the condenser surface upon dropwise condensation and the coefficients of heat transfer.( )

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