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AGEING STUDIES IN NUCLEATE POOL BOILING OF ISOPROPYL ACETATE AND PERCHLOROETHYLENE

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Abstract—Results are presented using a single, steam-heated, submerged tube for continuous periods of nucleate boiling up to 500 hr. The effects of different liquid/surface combinations were explored using perchloroethylene and isopropyl acetate boiling outside copper, mild steel and stainless steel tubes. Two different surface treatments were examined. From the results it has been confirmed that there can be a definite ageing process having the effect of reducing the heat flux with time. In specific cases, this ageing reduction may be masked for a time by interaction of surface and liquid tending to increase the heat flux.

Initially advantageous, the effects of surface treatment were rendered insignificant as the boiling proceeded.

It did not prove possible to correlate the time effects, but the results in general support and expand the ideas put forward by earlier investigators.

NOMENCLATURE

A, area of the heating surface [ft^2];
a, b, constants;
h_B, heat transfer coefficient [Btu/h ft^2 °F];
q/A, heat flux [Btu/h ft^2];
ΔT_B, boiling film temperature difference [degF];
t, time [h];
ΔTo, overall temperature difference [degF].

INTRODUCTION

An important variable which may affect considerably the heat transfer coefficient in nucleate pool boiling is the duration or history of the boiling, i.e. the "age" of the surface. The ageing of solid surfaces may be due to any or all of the following causes:

(1) Varying activity of minute pits, grooves and other small unwetted spots on the solid surface.
(2) Deposition of a fouling film on the heated surface.
(3) Corrosion of the surface.
(4) Temperature fluctuations during boiling.
(5) The gradual expulsion of dissolved gases from the liquid.
(6) The release of gases occluded on the solid surface.

The time elapse required to attain steady state heat transfer rates will vary, being affected by all these factors and other conditions such as the purity of the liquid, the material and the initial condition of the heating surface.

Jakob [1] first reported the ageing effect; subsequent studies have implied that the attainment of steady state heat transfer depends largely on the type of surface used, and to a lesser extent on its initial condition [2]. No general agreement, however, exists on the influence of heat flux on the ageing rate of a heating surface. In addition, rather little attention has been given to ageing in the boiling of organic liquids. In the chemical and petroleum industries the design of boiling equipment for organic liquids is of considerable importance, and the present work, therefore, used industrially important organic liquids in conjunction with common industrial heating surface metals to

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ascertain the changes in boiling heat transfer with time.

Studies were limited to moderate heat fluxes: it was not intended to investigate ageing effects near burnout, but in the range from just above incipient boiling up to peak heat flux for the liquids chosen, i.e. around 10^4–10^5 Btu/hft^2. This range of heat fluxes is reasonably representative of industrial practice. The main objectives were to investigate the effects,

(1) of different metals and surface conditions on the heat transfer–time relation;
(2) of different liquids on the ageing of particular surfaces;
(3) of different levels of heat flux on ageing.

THEORY AND CORRELATION

Recent trends in the extremely complex field of nucleate pool boiling favour a two-regime theory as suggested by Zuber [4]; a transition from an "isolated bubble" regime to a "bubble interference" regime occurring as temperature difference increases [7–10]. Jakob [1] seems to have been the first to attempt to correlate experimental boiling results using dimensional analysis, and many subsequent workers have explored the functional relation between the heat flux, q/A (or heat transfer coefficient, h_B) and the boiling film temperature difference T_B. Westwater [3] summarized the correlations available in 1961, showing the considerable measure of disagreement. Normally the slope reported for logarithmic q/A vs. ΔT_B plots is in the range 3 to 4, but figures from around unity for contaminated surfaces up to around 25 for very clean surfaces have been noted [5, 6]. There is little agreement between authors on the dependence of q/A on the physical properties of the system. It appears probable that the reason is the relatively small number of the possible variables that actually appear in the correlations. The omission of surface variables, e.g. the nucleation characteristics of the boiling surface, can be explained to some extent by difficulties of definition and measurement, and their apparent dependence on heat flux.

It seems that no simple correlation can apply over the entire nucleate boiling regime, with or without inclusion of a surface factor. Some of the equations suggested are derived from assumed models; but at present there is no convincing proof that any of these models is correct. In the present study no unambiguous measurement of nucleation site density was possible, and correlation of the experimental results has consequently been attempted in the conventional fashion, i.e.

$$q/A = a(\Delta T_B)^b$$

where the coefficient a must clearly be a function of the liquid/surface properties. In order to assess the ageing effects, the heat flux per unit area, q/A, or the heat transfer coefficient, h_B, was plotted against time.

APPARATUS AND PROCEDURE

The apparatus comprised a set of 7 identical boiler units of 2·4 l. liquid cpacity, each consisting essentially of a short horizontal copper shell, 6 in. i.d. × 10 S.W.G., containing a single offset $\frac{3}{4}$ in. o.d. × 16 S.W.G. steam heating tube. In process plant practice the materials most commonly employed for the heating tubes of boiling equipment are copper, mild steel and stainless steel; so tubes of these materials were used for the experiments. The total immersion length of the heating tube in each unit was $6\frac{1}{2}$ in., with a 3 in. test-section in the middle for measurement of the average tube wall temperature by the resistance thermometry technique. No subsidiary heaters were provided to keep the liquid at its saturation temperature: but each boiler was, of course, heavily lagged, using polyurethane foam insulation. The liquid level was kept approximately $2\frac{1}{2}$–3 in. above the heating tube to prevent any false effects due to proximity of the liquid surface to the heating surface [1, 11].

Figure 1 shows the flow diagram for a typical boiler in the set. Steam and steam condensate

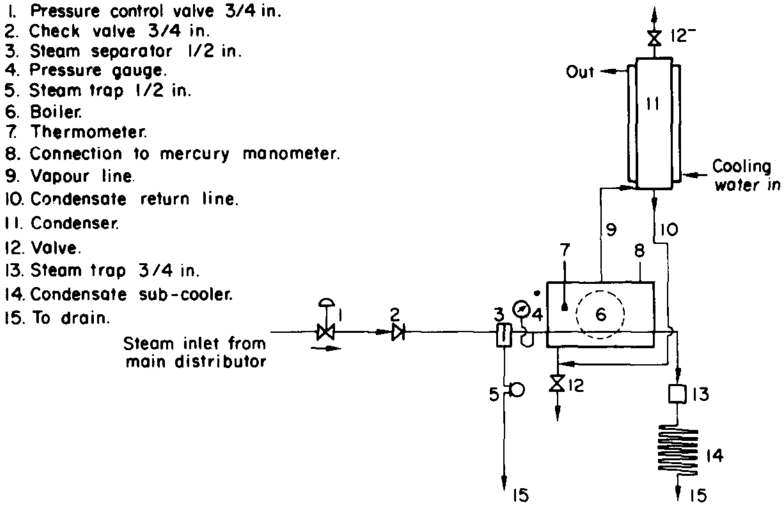

FIG. 1. Flow diagram of typical boiler.

arrangements were of conventional type, with independent control for each boiler. The vapour produced in each boiler was taken to a small (2 in. × 6 ft) single tube vertical water-cooled condenser vented at the top, the condensed liquid running back to the boiler by gravity.

The liquids chosen for the research programme were perchloroethylene and isopropyl acetate, the selection being mainly based on industrial importance, cheapness and ease of availability in bulk quantities; also, both were capable of being boiled at atmospheric pressure by the available steam supply.

Since one of the aims of the work was to simulate industrial conditions, no considerable surface preparation of the tubes was undertaken. To provide comparison with the results of other workers and to determine whether prior preparation of the surface could have a lasting effect, however, it seemed desirable to have results from tubes which had undergone some standardised surface treatment as well as from untreated tubes. Accordingly, runs included both "untreated" and "standard treated" tubes of each of the 3 metals. "Untreated" test sections were simply cut from tube stock, degreased and used. "Standard treated" sections were given a simple standard abrasive treatment after degreasing. Details are given in [2].

All tubes were examined under the microscope before and after each run. Before the run the surface texture of the untreated tubes varied widely; but generally, a few very large scratches of the order of 10×10^{-3} in. were noticed, while the shape and distribution of smaller imperfections were very irregular. Due to this non-uniformity, no measure of either size or density of imperfections was practicable. With standard treated tubes, before boiling, the scratches due to the abrasive treatment were of regular shape and parallel, width 1×10^{-3} in. or less. After boiling, all copper tubes showed a deposit of approximately 0·005 in. in the form of whitish or coloured patches. The mild steel tubes also showed small traces of deposit, but stainless steel showed none.

Before each test run the tubes were calibrated for resistance-temperature relationship. Steam was introduced into the heating tube at the predetermined pressure for each unit, and at least 2 hr continuous boiling was allowed before any data were collected. After the 2 hr initial period, figures were collected at every hour on the first day of the run, thereafter at intervals of 2–6 hr. Each run was carried on continuously for several days. The duration of run was increased from about 240 hr continuous boiling for the early runs to around 500 hr when it became apparent that in some cases ageing effects persisted beyond 250 hr. In all runs, both liquids and all three metals were used.

Control of boiling was by varying the steam pressure in the heating tubes: effectively, by varying the overall temperature difference, ΔTo. Two kinds of run were made to establish the time effects. The first kind was made at constant steam pressure such that the resulting heat flux was within the isolated bubble regime. In the second kind of run the steam pressure was cycled, that is, raised in steps of 2–10 psig (corresponding to ΔTo steps of 4–9°F) at fixed intervals and then lowered in steps of the same magnitude, data being recorded at each level. The purpose was to accelerate the ageing process for any given duration of test, since in this way a considerable part of any run was at the highest levels of ΔTo.

The steam pressures employed were limited to a maximum of 60 psig by the available supply: on the liquid side, all runs boiled at atmospheric pressure. The accuracy of the heat flux data, taking into account uncertainties in heat losses, the constancy and accuracy of steam pressure, errors due to condensate metering and hold-up of condensate in the tube was always within ±6 per cent.

Clearly, the average temperature of the heating surface is preferable to spot temperatures, and therefore the thermocouple technique was discarded in favour of D.C. resistance thermometry, using a section of the tube as the resistance (12–19). The electrical resistances of the test sections for the three tube materials were extremely small, ranging from 14 to 650 μ-ohm at 20°C, and from 21 to 800 μ-ohm at 160°C [2].

The maximum uncertainty in the tube wall temperature measurement was ±3·4°F for copper tubes, ±4·3°F for mild steel tubes and ±5·4°F for stainless steel tubes. From this point of view, in spite of the use of heavy-wall, industrial grade tubes, the accuracy of the present work is not inferior to that of previous workers.

RESULTS

The large quantity of data from the two kinds of run, and the number of combinations of metals, surfaces and liquids, renders the presentation of anything but typical sample data impossible in this paper: full results are given in ref [2].

The data collected were processed by a computer program [2], the principal parameters tabulated being the heat flux, q/A, the boiling film temperature difference, ΔT_B, and the corresponding heat transfer coefficient, h_B, at each time interval. A few typical curves are reproduced here, Figs. 2–7. The constant ΔTo runs were intended mainly to elucidate the course of the ageing effects, the cycled ΔTo runs to give better values for the final steady boiling of the fully aged surfaces. Results were plotted both for q/A against time, and h_B against time.

With the exception of copper/perchloroethylene, all surface–liquid combinations gave similar results, Fig. 2 being typical of constant

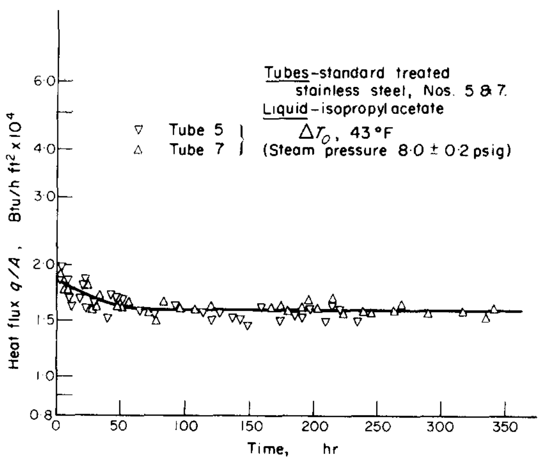

FIG. 2. Constant overall temperature difference runs: typical behaviour.

ΔTo runs, and Fig. 4 of cycled ΔTo runs. Generally, the heat flux/heat-transfer coefficient values fall off rapidly initially, then at decreasing rate, attaining stable values 10–50 per cent below initial figures 30–400 hr from commencement of boiling: in all cases the higher the temperature difference, the shorter the time elapse. Of the three metals, stainless steel showed the least ageing effect; at the highest temperature differences, boiling performance showed virtually no change with time in either liquid. In spite of the broad similarity of the curves, no general correlation either of q/A vs. t or h_B vs. t proved possible.

The copper/perchloroethylene system behaved differently, Figs. 3 and 5 being typical. All results for this system showed an initial increase with time (of up to 100 per cent), stabilising at a higher level after about 250 hr: the longer cycled ΔTo runs show that the values increased again for high ΔTo values after 350 hr, and were still increasing at the end of the runs, after 500 hr. The two curves of Fig. 3 show also the rather poor reproducibility of results with this system, much inferior to the other metal–liquid combinations.

The q/A vs. ΔT_B curves for the individual metals also show the small effect of pretreatment of the surface on the final boiling performance.

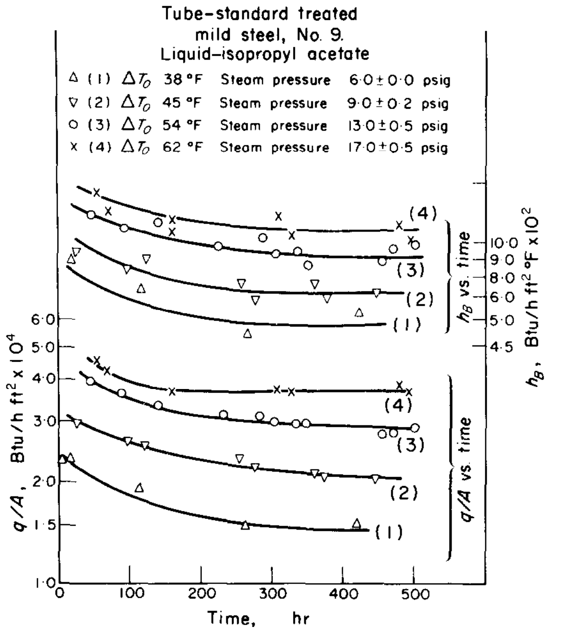

FIG. 4. Cycled temperature difference runs: typical behaviour.

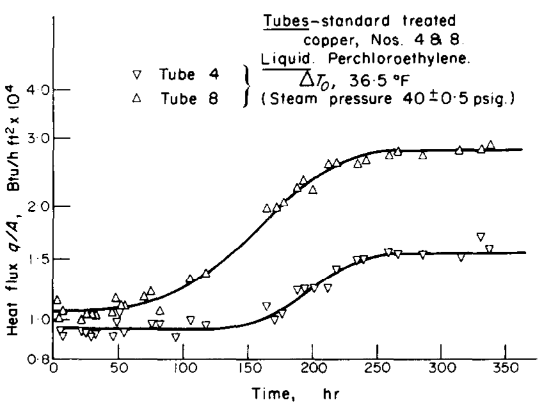

FIG. 3. Constant overall temperature difference runs: copper-perchloroethylene behaviour.

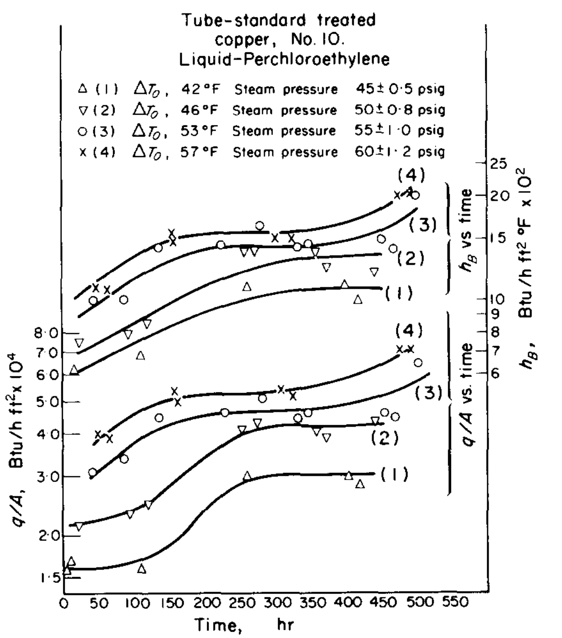

FIG. 5. Cycled temperature difference runs: copper-perchloroethylene behaviour.

Generally, standard treated tubes showed better boiling performance initially, but the effect faded rapidly: in many cases (see Figs. 6 and 7) the long term stable values were little different from those for untreated tubes. A feature of the results comparing different surfaces for the same liquid is that surfaces showing high q/A for given ΔT_B also show high slope b, Fig. 6.

CONCLUSIONS

(1) *Ageing*

The results of this work support the conclusion that the total ageing process comprises two sub-processes, one short term and the other long term.

The short term sub-process may terminate when initial high surface activity is diminished through decrease of nucleation caused by loss of adsorbed or trapped inert gas, or gradual expulsion of dissolved gas from the liquid, or through the rapid formation of a thin fouling film offering additional thermal resistance. In the long term, further decrease in the heat flux may be caused by reduced activity of the remaining stable nucleation sites, possibly through condensation of vapour trapped on the surface due to local temperature changes, or through formation of a compact deposit.

On this basis, it is also quite easy to postulate a "reverse ageing" process in which the heat flux is increased rather than decreased with passage of time. For example, slight pitting corrosion of the surface, or formation of patches of rough or porous deposit could serve to increase nucleation. Naturally, the type of solid and the nature of the liquid would be expected to determine whether and to what extent such reverse ageing occurred, and it would compete with the normal ageing processes already outlined. Corrosion theory suggests that copper-perchloroethylene would be more likely to react in this way than any of the other systems tested.

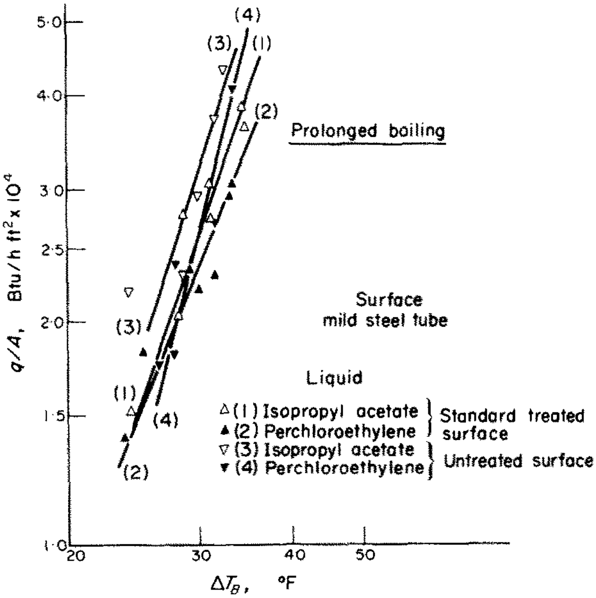

FIG. 7. Final heat flux/boiling film temperature difference: typical values for mild steel surfaces.

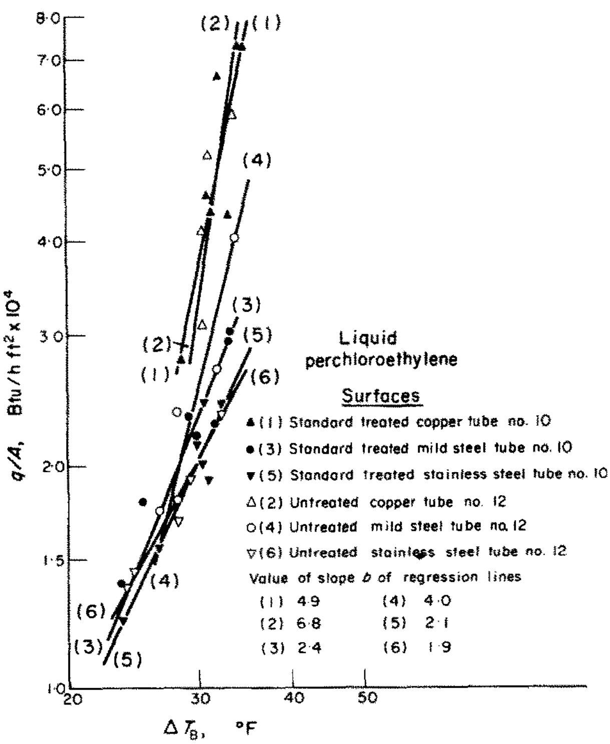

FIG. 6. Final flux/boiling film temperature difference: typical values for perchloroethylene with different surfaces.

It is concluded also that the higher the temperature difference, the less in general will be the ageing effect.

(2) *Effects of metal and liquid*

Differences of boiling behaviour occurred for different metals in the same liquid, and for the same metal in different liquids. On the whole, for a particular liquid, copper showed better results than mild steel, and mild steel than stainless steel. When different liquids were boiled over a particular metal, no definite conclusions could be drawn. Connection with liquid properties was suspected but could not be checked due to lack of data: at 68°F, the Prandtl numbers of the liquids were 7·45 for isopropyl acetate and 5·96 for perchloroethylene.

(3) *Effect of surface treatment*

In most combinations, the effect of surface treatment rapidly faded and became insignificant. For no obvious reason, the effect was more durable with mild steel tubes: nevertheless, there seems little point in abrasive cleaning of tubes for boilers.

(4) *General*

This present work seems to be the first in which stable values of boiling coefficients have been reported for different metal–liquid combinations after a sustained period of boiling. Consequently, the quantitative comparison of these results with those of other workers has not proved possible: in general, however, the findings agree well with the results reported by several authors [5, 6, 11, 20, 21] using similar tube materials.

The order of magnitude of the boiling coefficients recorded in this study was about the same as shown in industrial reboilers rather than the high experimental values reported by some workers. Over the periods studied, the ageing effect reduced the initial values by a maximum of 30–50 per cent: the final values recorded were reasonably stable. Possibly the most unexpected feature of the work was the results for the copper-perchloroethylene combination, which indicate that in circumstances where mild corrosion or precipitation are likely, the ageing effect may be completely swamped, producing a considerable increase in boiling in studies of this length.

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Résumé—On présente des résultats pour l'utilisation d'un tube submergé unique chauffé par la vapeur pour des périodes continues d'équllition nucléée allant jusqu'à 500 heures. Les effets de différentes combinaisons liquide/surface ont été explorés en employant l'ébullition du perchloro–éthylène et de l'acétate d'isopropyle en dehors de tubes de cuivre, d'acier doux et d'acier inoxydable. On a examiné deux traitements de surface différents. Il a été confirmé à partir des résultats qu'il peut y avoir un processus bien déterminé de vieillissement ayant pour effet de réduire le flux de chaleur avec le temps. Dans des cas spécifiques, cette réduction due au vieillissement peut être masquée pendant un certain temps par l'interaction entre la surface et le liquide tendant à augmenter le flux de chaleur. Les effets du traitement de surface, initialement avantageux, ont été rendus insignifiants lorsque l'ébullition s'est produite.

Il n'a pas été possible de corréler les effets du temps, mais les résultats corroborent en général et développent les idéés exposées dans des recherches antérieures.

Zusammenfassung—Es werden Ergebnisse von Langzeitversuchen bis zu 500 Stunden von Blasensieden an einem dampfbeheizten, eingetauchten Einzelrohr angegeben. Die Wirkungen verschiedener Kombinationen von Flüssigkeit und Heizfläche wurden untersucht, indem Perchloräthylen und Isopropylacetat, die an der Aussenseite von Kupfer-, Weichstahl- und rostfreien Stahlröhrchen siedeten, verwendet wurden. Es wurden zwei verschiedene Behandlungsmethoden der Oberfläche untersucht. Die Versuche haben bestätigt, dass ein definierter Alterungsprozess auftreten kann, der eine Verkleinerung des Wärmestroms mit der Zeit bewirkt. In besonderen Fällen kann diese alterungsbedingte Abnahme des Wärmestroms für gewisse Zeit durch eine Wechselwirkung von Oberfläche und Flüssigkeit, mit der Tendenz den Wärmestrom zu erhöhen, überdeckt werden.

Oberflächenhandlungen, die sich anfangs vorteilhaft auf den Wärmeübergang auswirkten, wurden mit zunehmender Siededauer unerheblich.

Es war nich möglich, den Zeiteinfluss durch eine Gleichung darzustellen. Im allgemeinen bestätigen und erweitern aber die Versuche die Überlegungen, die von anderen Autoren in früheren Arbeiten geägssert wurden.

Аннотация—Приводятся данные о длительном (до 500 часов) пузырьковом кипении с использованием единичной нагреваемой паром затопленной трубы. Исследовалось влияние различных комбинаций жидкости и поверхности при кипении тетрахлорэтилена и изопропилацетата снаружи медной трубы и труб из мягкой и нержавеющей стали. Изучено влияние двух видов поверхностной обработки труб. Результаты подтвердили, что происходит определенный процесс старения, который со временем уменьшает тепловой поток. В известных случаях этот процесс может быть некоторое время незаметен из-за взаимодействия поверхности с жидкостью, создающего тенденцию к увеличению теплового потока.

Хотя вначале и выгодное, влияние обработки поверхности становилось затем (по мере продолжения процесса кипения) незначительным.

Оказалось невозможным скоррелировать эффекты времени, но в общем результаты подтверждают и расширяют идеи, выдвинутые предыдущими исследователями.