HEAT TRANSFER IN DROPWISE CONDENSATION-PART II

SURFACE CHEMISTRY

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Abstract—A study of heat transfer in dropwise condensation in relation to surface chemistry showed that the steamside heat-transfer coefficient increased in the promoter series dibenzyl disulphide < dioctadecyl disulphide < montan wax, montanic acid. The coefficient was little effected by varying the amount of adsorbed montanic acid-19,20-T(n) from 0.5 to 11 equivalent monolayers. Roughening the surface slightly reduced the coefficient. Under comparable conditions, lower coefficients were obtained with stainless steel than with copper. Addition of oxygen to the steam rapidly produced filmwise condensation on copper surface; dropwise condensation could be restored by injecting carbon dioxide.

INTRODUCTION

THE AIM of this work was to compare the influence of physical and chemical variables on heat transfer in dropwise condensation. In Part I [1] the effects of heat flux, steam velocity and noncondensable gas concentration were described for the system copper-montan wax. The present work reports the results for several promoters and two substrates (copper and stainless steel). Surface roughness and the amount of adsorbed promoter (as measured by radioactive tracer techniques) were also varied. Results were obtained at constant steam velocity and in the virtual absence of non-condensable gas. Of these variables, only the promoter has been previously investigated [2, 3].

EXPERIMENTAL DETAILS

The basic procedure and apparatus were described in Part I [1]. Further details of surface finish and promotion are given below:

Surface finish

In addition to the standard surface finish (diamond pastes to $\frac{1}{10} \mu$ followed by electrodegreasing) the following alternative finishes were also used:

polishing stopped at 6 μ diamond, followed by electro-degreasing; surface abraded with grade

00 emery paper (grain size $\leq 89 \mu$), followed by electro-degreasing;

surface abraded with grade F emery paper, followed by electro-degreasing; surface etched with a chromic acid polishing solution; and standard surface oxidized during filmwise condensation by introducing 600 ppm of oxygen into the steam until tarnishing occurred (about 3 h).

Whereas the standard surface had a bright mirror-like finish, the abraded surfaces were matt and visibly scratched. Grain boundaries were visible under the microscope after the etching treatment. The oxidized surface was somewhat matt, the colour corresponding to the first interference colour (oxide layer about 350 Å thick). Bright and abraded surfaces would also have been covered with a thin oxide layer, formed by exposure to the air.

Promotion

Surfaces were promoted by adsorption from solutions at 30°C as follows:

Stearic acid: 10^{-3} to 10^{-2} M in benzene for periods of 5 to 30 min;

Montanic acid: 10^{-4} to 10^{-3} M in benzene for periods of 5 to 60 min;

Dioctedecyl disulphide: 10^{-3} or 2×10^{-2} M in carbon tetrachloride for 30 min;

Dibenzyl disulphide: 2×10^{-2} M in benzene for 30 min.

In each case the surface was rinsed with clean solvent after promotion. Radioactive stearic and montanic acids were used, the amount of promoter on the surface both before and after an experiment being measured by carbon 14 or tritium counting in a gas-flow proportional counter. Results are expressed in terms of an equivalent monolayer. By this is meant the amount of material equal to that in a Langmuir monolayer deposited over the condensing surface. The count rate for Langmuir monolayers of stearic and montanic acids was determined experimentally so that, by comparison, the count rate from a surface promoted by adsorption could be directly converted to equivalent monolayers. The word "equivalent" is intended to indicate that the detailed distribution of promoter adsorbed from the solution was not known.

Materials

Stearic acid-1-C14 with a specific activity of 4.3 mc/mmole and a radiochemical purity of 97-100 per cent was obtained from the Amersham Radiochemical Centre. Montanic acid-19.20-T(n) with a specific activity of 6.7 mc/mmole was prepared by the Kolbe synthesis from stearic acid - 9.10 - T(n). sample of dioctadecyl Α disulphide was obtained from the National Engineering Laboratory (N.E.L. promoter DP 75/55). Reagent grade dibenzyl disulphide was used without further purification. The stainless-steel rod was of Firth-Vickers Staybrite F.D.P. steel, code No. B.S: En 58B, the thermal conductivity of which was given as § 10.88 Btu/ft h degF. Cylinder oxygen and carbon dioxide were used without further purification. Solvents were of analytical reagent grade; benzene was further purified by passage through activated alumina.

RESULTS AND DISCUSSION

The results reported here were obtained at constant steam flow $(1.9 \text{ ft}^3/\text{min} \text{ through the cell})$ and, as discussed in Part I [1], are believed to be free from any diffusional resistance arising from the presence of non-condensable gas. Under these conditions it was found that both the

promoter and the surface effected the heat transfer. In all the experiments reported below, the whole of the condensing surface showed dropwise condensation except when otherwise noted.

The promoter

Type. Results are presented in Fig. 1 for the variation of ΔT (the difference between steam temperature and extrapolated surface temperature) with heat flux for several promoters on copper surfaces prepared by the standard procedure. The differences between promoters were quite distinct, becoming more obvious with increasing heat flux. At a flux of 150 000 Btu/ft²h, the coefficients were as follows: montan wax, montanic acid 53 000; dioctadecyl disulphide 42 000; and dibenzyl disulphide 35 000 Btu/ft²h. In all cases the coefficients decreased with decreasing heat flux [1].

The life of stearic acid on a standard copper surface was too short to allow the full heat flux



FIG. 1. Variation of ΔT with heat flux for several promoters on copper.





(i)



(11)





FIG. 2. Influence of excess promoter on heat transfer.

(i) and (ii): copper + 37.8 eq. monolayers of stearic acid, $\frac{3}{4}$ and 7 mins from the start of condensation: flux 177 000 and 178 000 Btu/ft²h; ΔT 6.0(3) and 5.0(4)°F; coefficients 29 400 and 35 400 Btu/ft²h degF respectively.

(iii) and (iv): copper + dioctadecyl disulphide (adsorbed from 2×10^{-2} M soln), $\frac{1}{2}$ and 56 min from the start of condensation: 175 000 and 181 000 Btu/ft²h, ΔT 6.6(1) and 3.7(8) degF; coefficients 26 500 and 48 000 Btu/ft²h degF respectively.

FIG. 6. Effect of oxygen on dropwise condensation (copper + montanic acid).

(i) steam only. (ii)-(iv) steam + 500 ppm O₂ at 45,
70 and 120 s respectively after introduction of oxygen. Flux and coefficients (i) 182 000 Btu/ft²h and 46 000 Btu/ft²h degF; (iv) 127 000 Btu/ft²h and 2900 Btu/ft²h degF.

range to be investigated. Longer lives were obtained on etched surfaces and, as seen in Table 1 below, similar coefficients were obtained for stearic and montanic acids on such surfaces.

Amount. The amount of fatty acid adsorbed on copper surfaces was varied (a) by varying the adsorption conditions and hence the initial coverage; (b) by the desorption of promoter accompanying condensation. In neither case was the heat-transfer coefficient significantly altered over the range of 0.5 to 11 equivalent monolayers. For amounts of promoter below about 0.5equivalent monolayers, condensation was largely or completely filmwise from the beginning. With more than about 20 monolayers, the coefficient was initially somewhat reduced and *increased* as desorption proceeded.

The results of varying the initial coverage are given in Table 1. Readings were taken as soon as possible after admitting steam to the cell; the times are given in column 3.

It may be seen from Table 1 that no regular change in coefficient occurred as the amount of promoter was varied between 0.5 and 11 equivalent monolayers. Etched surfaces gave lower coefficients than polished surfaces in agreement with the effects of roughening reported below. The similarity of results for stearic and montanic acids on etched surfaces has already been noted.

Somewhat lower values of the coefficient were obtained initially when excessive amounts of fatty acids were adsorbed. This may be seen in Table 1 for 22 equivalent monolayers of stearic acid, the lower value being associated with the appearance of enhanced wettability of the surface (cf. Fig. 2 (i)). In this latter example 38 monolayers of stearic acid were initially present. After condensation for 7 min the appearance of the surface improved and the coefficient increased (cf. Fig. 2 (ii)). This change was attributed to the desorption of excess disordered promoter.

Measurement of the amounts of promoter remaining on the surface after varying periods of condensation showed that desorption was occurring, as illustrated in Fig. 3. Stearic acid was lost from the surface more rapidly than montanic and this was believed to be the main

System	Initial coverage	Time (min)	ΔT, (degF)	Heat flux, (Btu/ft ² h)	Coefficient, (Btu/ft ² h degF)
Montanic acid-					
copper (standard prepn)	1.17	6	3.2	178000	55600
	1.20	7	3.8	173000	45600
	1.25	3	3.4	181000	53300
	1.38	4	3.4	181000	53300
	1.60	7	3.8	173000	45600
	1.93	5	3.4	195000	57400
Montanic acid-					
copper (etched)	0.54	5	4.9	180000	36800
	0.90	10	4.6	174000	37800
	1.85	5	4.8	193000	40200
	3.57	6	4∙6	177 000	38500
Stearic acid-					
copper (etched)	2.62	4	4.9	173000	35300
	2.9	7	4.4	182000	41400
	7.95	10	4.6	175000	38100
	11.04	4	4.4	175000	39800
	22.2	2	6.0	176000	29400

Table 1. Heat transfer as a function of coverage

* Equivalent monolayers



FIG. 3. Desorption of stearic and montanic acid from copper surfaces during condensation: surfaces prepared by standard procedure.

Inset: steamside heat-transfer coefficient as a function of the area of filmwise condensation—results obtained during the desorption of montanic acid from a copper surface.

cause of its shorter life. With montanic acid it was possible to make measurements of the surface temperature (at constant waterside conditions) for periods of up to 2 h. Although extensive desorption (up to 70 per cent) occurred during this time only slight changes were observed in surface temperature (a decrease of 10 per cent or less) provided that no areas of filmwise condensation appeared. This was further evidence of the insensitivity of the steamside coefficient to the amount of promoter at lower coverages. When, as a result of desorption, areas of filmwise condensation did appear the coefficient fell in the manner indicated by the curve inset in Fig. 3.

Although direct measurements were not made of the amounts of adsorbed sulphide promoters, there was indirect evidence that excess promoter reduced the heat-transfer coefficient. Promotion of a copper surface by a concentrated solution $(2 \times 10^{-2} \text{ M})$ gave an initial coefficient of 27 100 Btu/ft²h degF (at a flux of 173 000 Btu/ft²h) which gradually increased over a period of 60 min of. continuous condensation to a value of 44 700 Btu/ft²h degF. Surfaces promoted by adsorption from more dilute solutions (10⁻³ M) gave maximum values within 6 min of starting condensation. In the case of the sulphide promoters the increase in the steamside coefficient was not accompanied by any change in the appearance of the surface, as may be seen by comparing photographs (iii) and (iv) in Fig. 2.

These last results and the differences between promoters could be explained by postulating that the amounts of sulphide promoters adsorbed on copper were sufficient to introduce a thermal resistance. Assuming the thermal conductivity of dioctadecyl disulphide to be the same as for stearic acid (0.092 Btu/ft h degF), an increase in coefficient from 27 000 to 45 000 Btu/ft²h degF would correspond to the desorption of about 200 molecular layers of promoter (each 20 Å thick). The difference between dioctadecyl disulphide and montanic acid, 42 000 to 53 000 Btu/ft²h degF at a flux of 150 000 Btu/ft²h, would indicate a layer of sulphide promoter about 70 molecules thick. It may be noted that extensive adsorption of sulphur-containing compounds on copper has been reported [4].

Even with excessive amounts of adsorbed sulphide promoter, the grade of dropwise condensation was always found to be good. This was not so for fatty acids, excess material leading to the appearance of increased wettability (cf. Fig. 2). It is suggested that this excess fatty acid was in a disordered condition with hydrophilic carboxyl groups oriented towards the steam. Desorption of such material might be expected to leave behind a more hydrophobic surface in which carboxyl groups are preferentially attached to the copper surface. It would thus appear that the nature and amount of promoter may affect heat transfer either by introducing a thermal resistance or by increasing the wettability of the surface. These factors may reduce the value of the coefficient at high heat fluxes from about 50 000 Btu/ft²h for well-ordered promoter layers about one molecule thick to around 20 000 Btu/ft²h degF on surfaces with excessive amounts of promoter.

The surface

The influence of the surface on dropwise condensation was investigated (i) by comparing copper and stainless steel; (ii) by abrading a copper surface, and (iii) by oxidizing a copper surface. With montanic acid as promoter, stainless steel gave markedly lower coefficients than did copper. Abrasion and oxidation affected the heat transfer mainly by causing filmwise condensation.

Surface material. Results for stainless-steel and copper surfaces prepared by the standard procedure and promoted with about one monolayer of montanic acid are presented in Fig. 4. The low thermal conductivity of the steel limited



FIG. 4. Heat transfer during dropwise condensation on stainless steel and on copper promoted by montanic acid: initial coverage 1.97 and 1.93 equivalent monolayers respectively.

the maximum heat flux which could be obtained through a 2-in. bar with present waterside conditions to about 10 000 Btu/ft²h. Over the range of flux investigated it was found that the values of the coefficient were lower than for copper and decreased from about 8500 Btu/ft²h degF at a flux of 10 000 Btu/ft²h to a value of 2500 Btu/ft²h degF at a flux of 1000 Btu/ft²h.

The lower coefficients on stainless steel were not associated with any difference in the appearance of the condensing surfaces. In as much as all the other known variables were held constant the difference is attributed to a specific influence of substrate on the interfacial processes which determine heat transfer. Such a difference could arise from the influence of adsorption properties and surface free energy of the interface on the initial stages of the condensation cycle.

Surface finish. Results are presented in Fig. 5 for ΔT as a function of heat flux for copper surfaces of different finish. Heat transfer for

condensation on a surface with 6 μ diamond finish was closely similar to that for the standard finish. Etched surfaces and those finished with grade 00 emery gave somewhat higher values of ΔT . Even on these obviously roughened surfaces the coefficients were high. Thus, at a flux of 150 000 Btu/ft²h the value was 36 000 Btu/ft²h degF. This may be compared with 50 000 Btu/ft²h degF on a standard surface. It was not found possible to promote complete dropwise condensation by adsorption of montanic acid on copper surfaces abraded with grade F emery.

The amount of adsorbed montanic acid increased slightly with increasing surface roughness. Thus, after adsorption for 30 min from a 10^{-3} M solution the following average values were obtained: standard finish, 1.33; etched, 1.85; grade 00 emery paper, 2.13; and grade F emery paper, 1.74 equivalent monolayers.

The investigation of surface finish was undertaken in the hope of clarifying the mechanism



FIG. 5. The effect of surface finish on heat transfer.

of dropwise condensation. If, as has been suggested, the mechanism involves the drainage or fracturing of thin layers of water (of the order of 1 μ in thickness), variation of surface finish might be expected to interfere significantly with the process. The fact that high coefficients were obtained over the range of finishes examined would suggest that the processes critical for heat transfer occur on a scale well below 0·1-1 μ . The difficulty of promoting surfaces abraded with F emery appeared to arise from retention of water in the scratches by capillarity, a relatively gross effect.

Surface corrosion. Oxygen was found to have a deleterious effect on dropwise condensation on copper surfaces. If present in the steam it caused a rapid and permanent reversal to filmwise condensation, while prior oxidation of a surface rendered it difficult to promote.

(a) Oxygen in the steam. As shown in Part I, the addition of nitrogen or carbon dioxide to the inlet steam caused a marked reduction in heat transfer by introducing a diffusional resistance but produced no lasting effect. Oxygen, in addition to creating a diffusional resistance, produced on copper surfaces a permanent decrease resulting from the development of areas of filmwise condensation. The accompanying changes in the appearance of the surface are illustrated in Fig. 6 (i-iv). The development of filmwise condensation was accompanied by darkening of the surface, indicative of oxidation. The rate at which filmwise condensation developed increased (a) with increasing oxygen concentration in the range 50-600 ppm; and (b) with increasing heat flux, for a fixed oxygen concentration. Susceptibility to oxygen attack depended on the promoter. Surfaces promoted by fatty acids were more sensitive than those promoted by sulphides, and those promoted by 10-3 M dioctadecyl disulphide solutions were more susceptible than than those promoted by a 2×10^{-2} M solution. Promotion by this last solution gave surfaces that were unaffected by 600 ppm of oxygen over long were periods and which would give dropwise condensation after being exposed to moist air overnight. This latter treatment always produced filmwise condensation on copper surfaces promoted by fatty acids.

Measurements of the amount of fatty acid

promoter remaining on surfaces that had reverted to filmwise condensation under the influence of oxygen showed that desorption had not been accelerated by this treatment. The amount remaining generally exceeded the minimum required to produce dropwise condensation on bright polished surfaces—about 0.5 equivalent monolayers. Thus the effect of oxygen could not be attributed to loss of promoter.

(b) Oxidized surfaces. An alternative explanation of the effect of oxygen might be based on the further growth of an existing oxide layer. This could increase the wettability of the surface both by burying adsorbed promoter molecules and by creating fresh unpromoted surface. The properties of oxide layers were further investigated by pre-oxidizing copper surfaces during filmwise condensation to give oxide layers about 350 Å thick. Somewhat unexpectedly the adsorption of montanic acid on such layers was only slightly greater than on a polished surface-1.7 compared with 1.3 equivalent monolayers in 30 min from a 10⁻³ M solution. Condensation on oxide surfaces with this amount of promoter was largely filmwise from the beginning, becoming completely so within 10 min. At this time 50 per cent of the promoter remained.

These results indicated that for dropwise condensation more promoter was required on oxidized than on standard surfaces. This was demonstrated by the following experiment in which dropwise condensation and a high heattransfer coefficient were obtained on an oxidized surface by applying sufficient promoter. It was also shown that hydrophobicity could be restored to an oxidized surface with too little adsorbed promoter for dropwise condensation by dissolving away the oxide layer with carbon dioxide. These findings are presented in Fig. 7.

An oxidized copper surface was promoted with 22.2 equivalent monolayers of montanic acid by evaporation of a known volume of a standard solution. Condensation was initially mixed filmwise and dropwise, becoming completely dropwise in 5 min to give a maximum coefficient of 36 000 Btu/ft²h degF. This value persisted for about 1 min after which filmwise areas began to appear, growing to cover the whole surface after a total time of 36 min. The coefficient had then fallen to the filmwise value of 3000 Btu/ft²h



FIG. 7. Variation in steamside coefficient (for fixed waterside conditions) as a result of introducing oxygen and carbon dioxide into the system copper + montanic acid (22.2 equivalent monolayers).

degF. The initial growth of dropwise condensation was attributed to the removal or re-orientation of excess promoter to form, briefly, a wellpromoted hydrophobic surface; the subsequent appearance of filmwise condensation would then be explained by further loss of promoter by desorption.

At this point (38 min) carbon dioxide (600 ppm) was added to the steam. This resulted in an immediate but slight fall in coefficient followed by a gradual rise. The rise was accompanied by the reappearance of dropwise condensation, which completely covered the surface after a total time of 60 min. During this second stage 25 μ g of copper were dissolved compared with 2.2 μ g in the first stage when carbon dioxide was absent. The dissolution of copper by the carbon dioxide was accompanied by brightening of the surface, the amount removed corresponding to a layer of cuprous oxide 160 Å thick.

At a total time of 70 min the value of the co-

efficient was low (8000 Btu/ft²h degF) despite complete dropwise condensation. This was due to a diffusional resistance as shown by the increase to a value of 40 000 Btu/ft²h degF when the carbon dioxide supply was cut off.

The oxidation-dissolution cycle was then repeated by admitting oxygen at 88 min. The immediate fall in coefficient to 28 500 Btu/ft²h degF was followed by a slower decline to 20 700 Btu/ft²h degF as about 10 per cent of the surface reverted to filmwise condensation. The oxygen supply was stopped and the coefficient rose to 35 500 Btu/ft²h degF—àbout 90 per cent of the maximum value. This maximum value was restored by further treatment with carbon dioxide. At the end of the experiment (110 min), 0.84 equivalent monolayers of montanic acid remained on the surface.

This experiment served to confirm the view that the action of oxygen in producing filmwise condensation could be explained by postulating the formation of oxide layer which obscured promoter molecules already present and created fresh unpromoted surface. Dissolution of the oxide restored hydrophobicity by re-exposing promoter. An oxide layer could itself be made hydrophobic by applying sufficient promoter.

These findings throw some light on the difficulty frequently experienced in promoting dropwise condensation on surfaces that have become roughened and oxidized over long periods of operation. Gross roughening assists wetting by capillarity and oxide layers require relatively large amounts of promoter to render them hydrophobic. The greater facility with which bright metal surfaces can be promoted makes the initial removal of an oxide crust desirable. One way of doing this might be to inject small concentrations of carbon dioxide into the inlet steam.

To summarize, it may be said that for copper, surface chemical factors were found to be primarily important in determining the occurrence, extent and duration of dropwise condensation. Once dropwise condensation was established, their further variation always give heattransfer coefficients in excess of 20 000 Btu/ft²h degF. In contrast to this the combined effects of heat flux, non-condensable gas and steam velocity could produce a tenfold variation in coefficient, as was shown in Part I. In view of this, the wide range of coefficients as reported in the literature [1] most probably results from differences in these latter variables rather than in surface chemistry of the systems studied.

CONCLUSIONS

From a study of heat transfer during the dropwise condensation of steam on copper and stainless-steel surfaces it is concluded that:

- (i) The heat-transfer coefficient decreases in the promoter series montan wax, montanic acid > dioctadecyl disulphide > dibenzyl disulphide, on copper.
- (ii) Variation in the amount of fatty acid promoter on copper surfaces from 0.5 to 11 equivalent monolayers caused no significant variation in heat transfer. At lower coverages condensation was filmwise. At higher coverages wettability was somewhat increased by disordered excess promoter.
- (iii) Variation in surface finish from $\frac{1}{10}\mu$ diamond polish to grade 00 emery caused the coefficient to fall by about 30 per cent.
- (iv) Lower coefficients were obtained for stainless steel than for copper, when promoted by montanic acid.
- (v) Oxygen in the steam caused dropwise condensation to revert to filmwise on copper promoted by fatty acids. This was attributed to the growth of an oxide layer. Removal of this layer by carbon dioxide attack restored dropwise condensation.
- (vi) More promoter was required to give dropwise condensation on an oxidized copper surface than on a bright polished surface.

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Résumé—Une étude du transport de chaleur dans la condensation par gouttelettes en relation à la chimie surface a montré que le coefficient de transport de chaleur du côté de la vapeur augmentait dans la série accélératrice bisulfure de dibenzyle < bisulfure de dioctadécyle < cire de montan, acide montanique. Le coefficient était peu affecté en variant la quantité d'acide montanique adsorbé-19,20-T(n) de 0,5 à 11 couches monoatomiques équivalentes. Le coefficient est légèrement réduit si l'on rend rugueuse la surface. Avec des conditions comparables, on avait obtenu des coefficients plus faibles avec de l'acier inoxydable qu'avec du cuivre. L'addition d'oxygène à la vapeur d'eau produisait rapidement de la condensation par film sur les surfaces de cuivre; la condensation par gouttelettes pouvait être réobtenue en injectant du gaz carbonique.

Zusammenfassung—Eine Studie des Wärmeüberganges bei Tropfenkondensation in Beziehung zur Oberflächechemie zeigte, dass die dampfseitige Wärmeübergangszahl in der Reihenfolge der Promotoren Dibenzyl-Disulphid \leq Dioctadecyl Disulphid \leq "Montanwachs", "Montansäure" zunahm. Die Übergangszahl wurde von dem sich ändernden Betrag von adsorbierter "Montan"-Säure–19,20– T(n) von 0,5 bis 11 gleichwertigen einmolekularen Schichten wenig beeinflusst.

Aufrauhen der Oberfläche verringerte die Übergangszahl unbedeutend. Unter vergleichbaren Bedingungen ergaben sich mit rostfreiem Stahl geringere Übergangszahlen als mit Kupfer. Zugabe von Sauerstoff zum Dampf ergab schnell Filmkondensation an Kupferoberflächen. Durch Zugabe von Kohlendioxyd konnte Tropfenkondensation wiederhergestellt werden.

Аннотация—Исследование теплообмена при капельной конденсации в зависимости от химического состава поверхности показало, что в ряду промоторов; бензиловый дисульфид, диоктодекановый дисульфид, монтановая кислота—коэффициент теплообмена со стороны пара возрастает.

Незначительное воздействие на коэффициент теплообмена оказывало изменение количества адсорбированной монтановой кислоты-19,20-*T*(*n*) от 0,5 до 11 эквивалентных мономолекулярных слоев. С увеличением шероховатости поверхности коэффициент несколько уменьшается. При сравнимых условиях коэффициенты теплообмена для подложки из нержавеющей стали меньше, чем для медной. Добавление к пару кислорода тотчас вызывало пленочную конденсацию на медной поверхности; капельную конденсацию на медной поверхности; капельную конденсацию можно было ывзвать, введя двуокись углерода.