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MEASUREMENT OF CONTACT ANGLES AND EVALUATION OF SURFACE COATINGS

by

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16. Abstract

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ABSTRACT

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SUMMARY

This report describes a program aimed at identifying stable surface treatments for 301 stainless steel, ASTM B-88-61 copper and 6061-T6 aluminum alloy which give high and stable equilibrium contact angles (θ) with water, methanol and Freon 11 (trichlorofluoromethane) at 20°C and at their respective normal boiling points in the presence of only the liquid vapor. A special environmental chamber in which θ could be measured at temperatures between 20° and 100°C in the presence of only the saturated vapor of the test liquid was used for measurements of θ for each of the three liquids on each of the three cleaned, polished metals at 20°C and their respective normal boiling points. Methods were developed for applying low energy coatings to the cleaned, polished metals, and metal-coating combinations were screened at 20°C for high θ and stable θ. On the basis of the results of the screening tests, nine metal-coating-liquid systems were selected for special study in the environmental chamber. For each system, θ was measured in the presence of only the saturated vapor of the liquid at 20°C and at the normal boiling point of the liquid. The measurements at the normal boiling point were extended over at least an 18-hour period.

Seven coating materials were used in the development of low energy surface treatments for the metals. These were the polymeric fluorocarbon materials, TE-3170 and FEP Teflon, and the fluorocarbon telomer Vydax 201G; the acrylic acid polymers or copolymers esterified with fluorinated alcohols, Zepel B and TLF-2475; and the lower molecular weight perfluorinated monolayer-forming compounds, TLF-1914 and perfluoro-octanoic acid. For the polymer-coated surfaces, the initial θ values for the liquids were in the ranges: water, 102-121°; methanol, 41-73°; and Freon 11, 0-30°. The results were more variable and generally less good for the TLF-1914 and perfluoro-octanoic acid coatings, but initial Freon 11 θ values of 40° were obtained on some TLF-1914 coatings. Judging from the θ values before and after 24 or 48-hour immersions in the boiling liquids, TE-3170 and FEP Teflon performed best with water and methanol. With Freon 11, no coating gave both a high and stable θ.

Of the nine systems selected for study in the environmental chamber, seven appeared to have good contact angle stability. These systems and the θ values at the boiling points were:

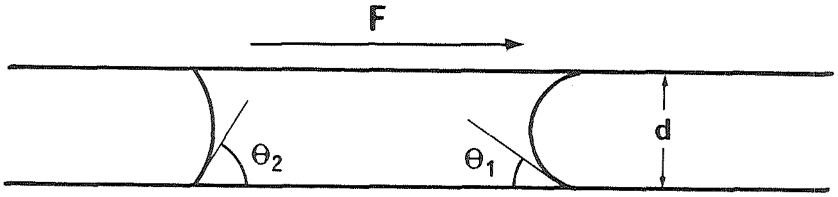
Metal	Coating	Liquid	θ (deg)
stainless steel	FEP Teflon	water	115
aluminum	FEP Teflon	water	116
copper	FEP Teflon	water	115
stainless steel	TE-3170	water	117
stainless steel	FEP Teflon	methanol	51
stainless steel	TE-3170	methanol	52
stainless steel	Vydax 201G	methanol	41

INTRODUCTION

In recent years, the heat pipe has become important as a device for the efficient transfer of heat, particularly in applications in which low weight and low volume are prime considerations. Improvements in the performance of heat pipes have generally been the result of changes in mechanical configuration and choice of working fluid (1). On the other hand, though surface phenomena associated with vapor condensation and liquid transport through the capillary system of the wick have been recognized as important factors, less attention has been focussed on them.

There appear to be two main ways in which the surfaces exposed to the working fluid in a heat pipe may affect the overall performance. They both involve solid-liquid-vapor contact angles. The first effect concerns the configuration taken up by the liquid as its vapor condenses on cold surfaces. Depending on whether the contact angle is zero or finite, the liquid will spread spontaneously over the surface as a continuous film or will form discrete, lens-shaped droplets which will only coalesce when they have grown sufficiently large. It is well known from heat transfer studies that the latter situation leads to more efficient heat transfer to a condensing surface (2). For this reason, treatment of the condensing surfaces in a unidirectional heat pipe so that they will give high contact angles with the liquid appears to offer hope for improved performance.

The second effect involving contact angles which may affect heat pipe performance concerns the transport of liquid from the cold end to the hot end through the wick. The driving force for the transport will be greatest if the contact angle at the hot end is zero while that at the cold end is the highest which can be achieved. While the quantitative effect will depend upon the exact geometry of the system, the concept can be illustrated by consideration of a capillary tube treated in such a way that one end has a contact angle θ_1 toward a slug of liquid contained within it, while the other end has a contact angle θ_2. Referring to the diagram below, if the surface



tension of the liquid is γ and the diameter of the tube is d, the driving force F tending to move the slug from left to right, from the region of higher contact angle to lower contact angle, is given by:

$$F = \pi d \gamma (\cos \theta_1 - \cos \theta_2)$$

Thus, it can be seen that, for given values of d and γ, the greatest conceivable value of F, and hence the greatest rate of flow of liquid of given viscosity, would be obtained if θ_1 were 0° and θ_2 were 180°. In reality, contact angles of 0° can be obtained but contact angles greater than 120° are seldom observed for any liquid other than mercury (3).

Because of the potential benefits for heat pipe performance, the work described in the present report was intended to identify stable surface treatments which would significantly increase the equilibrium solid-liquid-vapor contact angles for selected metal-liquid combinations which might be used in heat pipes. Three metals representative of construction materials for heat pipes and three liquids which might be used as working fluids in heat pipes were chosen for study. The metals were 301 stainless steel, ASTM B-88-61 copper and 6061-T6 aluminum alloy, and the liquids were water, methanol and Freon 11 (trichlorofluoromethane).

The work was divided into three tasks. Task I was the construction of an environmental chamber in which contact angle measurements could be made at temperatures between 20° and 100°C in the presence of the saturated vapor of the test liquid as the only vapor phase. This task also included the making of contact angle measurements for each of the three liquids on each of the three cleaned, polished metals in the presence of only the saturated vapor of the liquid at 20°C and at the normal boiling point of the liquid.

Task II comprised the development of methods for applying low energy coatings to the cleaned, polished metals and the screening of the metal-coating combinations for contact angle and durability.

Task III was the testing in the environmental chamber of nine metal-coating-liquid systems selected from those studied in Task II. For each system, contact angle measurements were made in the presence of only the saturated vapor of the liquid at 20°C and at the normal boiling point of the liquid, with the measurements at the normal boiling point being extended over at least an 18-hour period to provide information about the coating's durability.

The structure of the work plan is reflected in the structure of this report. Thus, after a presentation of background material relating to contact angles and surface coatings, individual sections are devoted to the three tasks. The report is concluded with a general discussion linking together the results of the tasks and a summary.

BACKGROUND

Much of our knowledge about contact angle relationships between solids and liquids is due to Zisman and his coworkers. Their work was reviewed by Zisman in 1964 (4). An important empirical concept pointed out by him is that of the critical surface tension, γ_c, of a solid surface. The γ_c value for a surface is, essentially, the lowest surface tension which a liquid could have without having a zero contact angle on the surface. γ_c values are determined experimentally. They provide a rough but useful guide to the prediction of spreading behavior.

In a number of cases, the contact angles θ of members of a homologous series of compounds can be expressed by:

$$\cos \theta = 1-k\ (\gamma_L-\gamma_c)$$

where k is a constant and γ_L ($>\gamma_c$) is the surface tension of the liquid; if $\gamma_L < \gamma_c$, $\cos \theta = 1$ and $\theta = 0°$. This suggests that the contact angle of a given liquid on a surface will be greater, the lower the value of γ_c.

The materials which, so far, have been found to have the lowest γ_c values are highly fluorinated organic polymers and lower molecular weight compounds made up predominantly of CF_2 and CF_3 groups.

Some γ_c values for various types of exposed surface groupings are shown in Table I. They suggest that, provided they are durable, coatings of highly fluorinated compounds are to be preferred for obtaining high contact angles. Such compounds, mostly polymers, were used in the present study (see Table II). They are often described as low energy coating materials because their interaction energies with adsorbed molecules are low.

TABLE I

CRITICAL SURFACE TENSIONS OF LOW ENERGY SURFACES
(from Zisman, ref. 4)

Surface constitution	γ_c (dynes/cm, 20°C)
$-CF_3$	6
$-CF_2H$	15
$-CF_3$ and $-CF_2-$	17
$-CF_2-$	18
$-CH_2-CF_3$	20
$-CF_2-CFH-$	22
$-CH_3$ (crystal)	22
$-CH_3$ (monolayer)	24
$-CF_2-CH_2-$	25
$-CFH-CH_2-$	28
$-CH_2-$	31

The low energy coating materials chosen for the present study represented the commercially available range of coating materials capable of giving surfaces containing only CF_2 and CF_3 groups while differing in molecular weight and in the presence or absence of polar groups. The latter are important in regard to the adhesion of the coating to the substrate.

As indicated in Table II, the coating materials were:

- TE-3170, a high molecular weight polytetrafluoroethylene
- Vydax 201G, a tetrafluoroethylene telomer
- FEP Teflon, a tetrafluoroethylene-hexafluoropropylene copolymer
- Zepel B, a polymer or copolymer of acrylic or methacrylic acid with perfluorinated side chains introduced by esterification; the molecular weight is about 25,000
- TLF-2475, a fluorinated material similar to Zepel B but of lower molecular weight
- TLF-1914, a perfluorinated compound of about 800 molecular weight containing a phosphoric acid grouping
- Perfluoro-octanoic acid, $CF_3 \cdot (CF_2)_6 \cdot COOH$

It was expected that, as indicated in Table II, the greater number of CF_3 groups in the last five materials would cause them to have lower γ_c values, and higher contact angles with the test liquids, than the two tetrafluoroethylene materials. (The properties of the liquids are summarized in Table III). Further, it was expected that the materials containing polar groups, whether acrylic, phosphoric or carboxylic, would bond more strongly to the metal substrates or to coatings, such as oxides or sulfides, which might be formed upon them by chemical treatment; therefore they might be expected to give more durable coatings. Lastly, it was expected that differences in chemical constitution and in molecular weight would lead to differences in ease of application and of obtaining uniform, continuous coatings over the metals.

TABLE II

PROPERTIES OF COATING MATERIALS

Name	Probable Chemical Type	Molecular Weight	Probable Surface Constitution	Form	Probable Critical Surface Tension (dyne/cm)	Melting Point (°C)	Supplier
Vydax 201G	TFE telomer[a]	ca. 3,700	$-CF_2-$	5μ dispersion in perchloroethylene	18[b]	323	du Pont
TE-3170	TFE polymer	ca. 2,000,000	$-CF_2-$	0.2μ aqueous dispersion	18[b]	335	du Pont
Teflon FEP	TFE-HFP copolymer[a]	ca. 250,000	CF_3- and $-CF_2-$	0.1-0.25μ aqueous dispersion	17[b]	270	du Pont
Zepel B	polymer or copolymer of acrylic or methacrylic acid esterified with a perfluorinated alcohol	ca. 25,000	$CF_3-(CF_2)_n-$	< 0.8μ aqueous dispersion	11[c]	270[d]	du Pont
TLF-2475	polymer or copolymer of acrylic or methacrylic acid esterified with a perfluorinated alcohol	< 25,000	$CF_3-(CF_2)_n-$	< 0.8μ aqueous dispersion	11[c]	250[d]	du Pont
TLF-1914	long chain fluorocarbon phosphate	ca. 800	CF_3-	waxy cream colored solid	6[b]	60	du Pont
Perfluoro-octanoic acid	$CF_3(CF_2)_6COOH$	414	CF_3-	colorless crystalline solid	7.9[e]	53	K&K Laboratories

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a. TFE = Tetrafluoroethylene; HFP = Hexafluoropropylene.

b. Values deduced from Zisman (ref. 4).

c. Values deduced from Bernett and Zisman (ref. 5).

d. Softening point; no sharp melting point observed.

e. From Hare, Shafrin, and Zisman (ref. 6).

TABLE III

PROPERTIES OF THE TEST LIQUIDS

Liquid	Composition	Vapor pressure at 20°C (torr)	Boiling Point (°C)	Surface Tension γ dynes/cm	Surface Tension T°C
Freon 11	CCl_3F	672[a]	23.77	18[a]	25
Methanol	CH_3OH	88.7[b]	64.96[c]	22.65 19.52	20 50
Water	H_2O	17.5	100	72.75 58.9	20 100

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a. Reference 7.

b. Reference 8.

c. Unless otherwise indicated, data are from reference 9.

The highest water contact angle observed by Shafrin and Zisman (3) was 120°. This was on the CF_3-rich surface of a polymethacrylic ester with perfluorinated side chains. A value almost as high, 118°, was obtained on an acrylic ester with perfluorinated side chains and on a monolayer of 11-(perfluorodecyl)-undecanoic acid. By analogy, we might expect contact angles in the 118° to 120° range to be obtained on the fluorinated acrylic materials, Zepel B and TLF-2475, and on perfluoro-octanoic acid and TLF-1914. Also, since Shafrin and Zisman found no water contact angle less than 108° on any homo- or copolymer exposing C and F atoms only, no water angle less than 108° would be expected for the coating materials used in the present study.

In regard to the expected contact angles of Freon 11 on the coating materials, it is relevant that Fowkes (10) has shown that if the solid-liquid interfacial forces are of the dispersion type, the contact angle can be expressed by:

$$\cos \theta = -1 + \frac{2\sqrt{\gamma_L^d \gamma_s^d}}{\gamma_L} - \frac{\pi_e}{\gamma_L} \qquad (1)$$

where γ_L^d and γ_s^d are, respectively, the dispersion force contributions to the liquid and solid surface tensions, γ_L is the liquid surface tension and

π_e is the spreading pressure which may be taken as zero when the contact angle is greater than zero. For a perfluorodecanoic acid monolayer on platinum, Fowkes found γ_s^d to be about 13 dynes/cm. If for Freon 11 (γ_L = 18 dynes/cm, ref. 7), as for many non-hydrogen bonded liquids, γ_L^d is equal to γ_L, it may be calculated from equation (1) that the contact angle of Freon 11 on the monolayer should be about 45°. Since the perfluorodecanoic acid monolayer provides a CF_3-rich surface, these considerations suggest that 45° is the order of magnitude of the maximum contact angle to be expected for Freon 11 on any surface.

Careful cleaning of metal surfaces to which coatings are to be applied is important if good adhesion is to be obtained. As with adhesive joints (4), the interface should be as free as possible from low energy surface films and dust. Procedures for cleaning metal surfaces were evaluated by Schwartz and Ellison as reported in an earlier NASA report (11). The best of these procedures, vapor degreasing followed by immersion in an alkaline cleaner and thorough rinsing with water, was adopted in the present work.

The measurement of the true contact angles of high surface tension liquids such as water on high energy surfaces such as metals is difficult because of the strong tendency of the metals to adsorb organic vapors. Even a small fraction of a monolayer of organic molecules appears to be sufficient to increase the contact angle of water on many surfaces (12), and Bewig and Zisman (13) state that a monolayer of a nonpolar organic compound such as hexane causes the water contact angle to be between 55 and 75°, depending on the metal surface.

There is an extensive literature on contact angle measurements and their interpretation. It covers such matters as the effects of surface roughness, temperature and chemical constitution upon contact angles, as well as reporting the results of measurements for specific solid-liquid systems. The literature will not be reviewed further here, though reference to relevant items will be made in the Discussion Section of this report.

TASK I - CONSTRUCTION OF THE ENVIRONMENTAL CHAMBER AND ITS USE IN MEASUREMENTS OF CONTACT ANGLES ON THE CLEAN METALS

The objectives of Task I were:

1. to design and construct an apparatus for the determination of contact angles at temperatures between 20° and 100°C in the presence of only the saturated vapor of the liquid.

2. to use the apparatus for the determination of the solid-liquid-vapor contact angles of distilled water, anhydrous methanol and Freon 11 on 301 stainless steel, ASTM B-88-61 copper and 6061-T6 aluminum alloy. For each solid-liquid combination, measurements were to be made at 20°C and at the normal boiling point of the liquid.

EXPERIMENTAL

Materials

The metals and liquids used in Task I are described in Appendix I. The appendix also describes the procedures used in grinding, polishing and cleaning the metal planchets upon which the contact angles were measured.

The Environmental Chamber

Details of the environmental chamber constructed in Task I (see Figures 1 through 4) are given in Appendix II. However, salient features of its design and operation will be pointed out here. In particular, attention will be drawn to details which had an important bearing on the ability of the chamber to perform as required. They concern the cleaning of the chamber, control of drop size, equilibrium between liquid and vapor, temperature measurements and the detection of air in the chamber.

a. Cleaning

As far as possible, the chamber was constructed of metals and ceramic materials. The exceptions were the Viton O-rings used in the seals and the Teflon insulation used on thermocouple wires. To minimize the likelihood of contamination of the chamber by dust or grease, the O-rings and Teflon-insulated wires were baked in a vacuum oven at 180°C for 6 hours to remove volatile materials while the other parts were vapor degreased with trichloroethylene. Assembly was carried out in the low dust environment of a Class 10,000 laminar flow hood in which the measurements were to be made. (Dust counts in the hood made at the start and end of the project showed it to be performing well within specifications.) The parts were handled with degreased forceps or clean gloves.

b. Control of Drop Size

The controlled formation of drops under the pressure difference between the outside atmosphere and the reduced pressure in the chamber at 20°C was made possible by reducing the effective internal diameter of the 0.012 cm i.d. (31 gauge) syringe needle through insertion of a length of 0.0102 cm diameter stainless steel wire which almost filled the bore.

c. Liquid-Vapor Equilibrium

The criterion of equilibrium between liquid and vapor was zero rate of evaporation. To achieve this for the small drops on the test specimens, it was essential that no surfaces within the chamber should be colder than the specimens and that sufficient liquid should have been introduced into the chamber for its vapor to fill the free space at the necessary pressure. If these conditions were not closely met, rapid evaporation of drops on the specimens could be observed.

To achieve the required control over the temperature distribution in the chamber, several steps were taken. The chamber was surrounded with polyurethane foam insulation with openings cut at the windows and where access was needed to the syringe controls, the stage control rods and the valve (see Appendix II and Figures 3 and 4). The windows and their flanges were insulated by closed air spaces formed by pieces of optically flat glass embedded in foam holders, while extensions of low thermal conductivity plastic were made to the syringe controls and the control rods; they could then be operated from outside of the layer of foam insulation. A foam plug was used to close the opening to the valve. The main heat supply to the chamber for measurements at 100°C was provided by circulation of a water-glycol solution at about 115°C through the heating coils but small electrical heaters or heating tapes were still needed for local heating at the points of highest heat loss. These points were at the valve, the windows, the control rods and the syringe. The stage carriage was modified to include a thermoelectric device the top surface of which, by adjustment of the current to the device, could be cooled by as much as 5°C to bring the stage to a temperature below that of the coldest point on the chamber walls. With this arrangement, it was possible to hold small water drops on the stage for many hours and to confirm, by the condensation which formed on lowering the stage temperature by less than 1°C, that the conditions were close to equilibrium.

d. Temperature Measurements

Three thermocouple junctions were used for monitoring temperatures within the chamber. One was attached to the stage, another to the stage carriage below the thermoelectric device, and the third to the center of the end plate carrying the control rods (see Appendix II and Figure 3). Using a sensitive galvanometer to measure the e.m.f., the temperature difference between any one of the three junctions and a reference junction attached to the bulb of a mercury-in-glass thermometer could be determined to within 0.07°C. It was estimated that the combined errors in determining the stage temperature should not have exceeded 0.2°C.

e. Checks for the presence of air within the chamber

The chamber could be evacuated to a pressure of 2×10^{-3} torr. After being closed off from the pump for a period of 20 hours, the extent of leakage into the chamber was checked by opening the valve to the evacuated but isolated manifold and McLeod gauge. The pressure was found to be 25×10^{-3} torr. An independent observation had shown the relative volumes of the chamber and manifold to be 1:3 so that actual build-up of pressure in the chamber over the 20 hours period could be calculated to be 100×10^{-3} torr. Other checks on the pressure of air in the chamber at various stages in the contact angle measurements gave pressures as high as 1 torr. In such cases, the chamber was momentarily opened to the pump and trap to remove the non-condensable gases with the vapor of the liquid in the chamber. This technique was effective in removing 99% of the air in a single step. A pressure of 10^{-2} torr of air in the chamber with the saturated vapor of the test liquid at the normal boiling point would imply that there was 1 molecule of air for every 38,000 molecules of the vapor. In the case of the same pressure of air in the chamber with saturated water vapor at 20°C, about 1 molecule in 1700 would be air.

Contact Angle Measurements

The environmental chamber was mounted on the bench of a contact angle goniometer (14) in place of the usual small cell. The objective lens of the goniometer telescope was chosen so as to allow a 9.5 cm working distance. This was necessary because of the impossibility of approaching closer than 6.5 cm to the center of the chamber. Seven repeated measurements on a single drop showed the standard deviation for measurement of a single angle to be about 0.8°.

Three freshly cleaned and polished planchets (see Appendix I), one of each metal, were placed on the stage of the environmental chamber (Figures 2 and 3) and the stage was remounted in the chamber. The syringe was filled with the freshly distilled test liquid and replaced in the top of the chamber. The chamber was then pumped out. The stage temperature was adjusted to 20°C and, after checking the pressure, the valve to the vacuum line was closed in preparation for introduction of the liquid. Liquid was fed slowly into the chamber from the syringe, drop formation at the needle tip being observed through the goniometer telescope. Initially, the drops issuing from the syringe "boiled" furiously and rapidly disappeared but, later, the drops became sufficiently long-lived to permit them to be transferred to the reservoir on the stage. Even then, the liquid still evaporated at a visible rate indicating that the vapor was not in equilibrium with the liquid. The evaporation of liquid in the reservoir cooled the stage thereby increasing the time taken to prepare for the first measurements. Finally, the point was reached where the drops no longer evaporated. The flow of liquid into the chamber was then stopped. If the planchet surfaces were wet with an excess of liquid, this was caused to evaporate by temporarily providing heat input to the stage through the thermoelectric device.

When the conditions in the chamber were judged satisfactory, a small drop of liquid was transferred from the syringe needle to a planchet, the behavior of the drop on the planchet being observed through the telescope. If the liquid spread rapidly and spontaneously across the surface, the contact angle was considered to be zero. If the liquid remained confined in a small area close to the needle, the contact angle was not zero and, after withdrawal of the needle, measurements of the angles on both sides of the drop were made. Usually, it took at least one hour from the time the planchets were placed on the stage until the measurements at 20°C could begin. The stage was then moved so that a second drop could be placed on an unwetted area of the planchet and its contact angles measured. The procedure was repeated several times on each of the three planchets. The chamber temperature was then raised to prepare for the measurements at the boiling point of the test liquid. (Due to slow temperature equilibration, at least five hours was required to change from 20° to 100°C.) Measurements at the boiling point were then made as for 20°C. In cases where the volume of liquid required exceeded the volume in the syringe, the syringe was refilled with freshly distilled liquid. This was done by removing the plunger and introducing the liquid into the top from a second syringe.

RESULTS

The results of the contact angle measurements on the cleaned, polished metal planchets are given in Table IV. While achievement of a temperature of 20°C on the stage gave no problem, difficulties were encountered in the precise attainment of the desired higher temperatures. The difficulties were due to slow temperature equilibration within the chamber.

The contact angles of methanol and Freon 11 on each of the three metals at 20°C and at, or close to, their respective boiling points were zero. The results for water were not so clear cut. Thus, the measurements at 20° and at 99°C showed low but non-zero contact angles on all three metals. Because of the lack of reproducibility, the results were merely recorded as the limits of the ranges in which the measurements on each metal fell. The

TABLE IV

CONTACT ANGLES (degrees) OF LIQUIDS ON CLEANED AND POLISHED METAL SURFACES IN THE PRESENCE OF PURE VAPOR AT 20°C AND CLOSE TO THE BOILING POINT

Metal	Contact Angle (degrees)							
	Freon 11		Methanol		Water[a]			
	20°C	23.7°C	20°C	60°C	20°C	99°C	106°C	101°C
Stainless steel	0	0	0	0	16-20	19-20	61-90	20-24
Copper	0	0	0	0	8-13	14-20	44-60[b]	23[b]
Aluminum	0	0	0	0	8-12	16-17	0-45[b]	--[b]

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[a] The planchets were polished and cleaned between each set of measurements at about 100°C. In addition, the environmental chamber was thoroughly cleaned following the measurements at 106°.

[b] Visible evidence of corrosion.

measurements were repeated after repolishing and cleaning the planchets. The temperature for the new set of measurements was 106°C and the contact angles were found to be higher than before. On removing the planchets from the chamber, the copper, and particularly the aluminum, showed signs of corrosion. The high angles suggested serious contamination so the chamber was degreased and provided with new, baked-out O-rings. A third set of measurements, this time at 101°C, gave lower contact angles in the 20-25° range, thereby suggesting that the contamination had been reduced. In view of Zisman's well substantiated view (4) that water, like most other simple liquids, should have a zero contact angle on all really clean metals, it was believed that some source of hydrophobic contamination still remained. However, because of the likely difficulties in completely avoiding contamination in the environmental chamber, it was decided to conclude Task I at this point and to make the chamber available for the Task III studies of low energy coatings. At the end of Task III, one further set of measurements was made with water on two cleaned, polished, stainless steel planchets at 20° and 100°C. These are reported in Table XII. The fact that the water contact angles at 100°C after 45 hours in the chamber were about 25° indicated that there had been no increase in the degree of contamination throughout the period of Task III.

TASK II - SURFACE TREATMENT STUDIES

Task II was carried out simultaneously with Task I. The task had two objectives:

1. to determine methods of altering the surface energy of the three metals so that significant increases in the solid-liquid-vapor contact angles for the three liquids at the pressures and temperatures specified for Task I could be realized.

2. to evaluate the stability of the surface treatments and to determine their effects on the solid-liquid-vapor contact angles by measurement of contact angles at ambient temperature and pressure.

The work in Task II consisted of three parts - the application of selected surface treatments and coatings to the metal planchets; measurement of contact angles on the coated metals; and accelerated durability testing of the coatings by measuring the contact angles again after immersion of the planchets in refluxing solvents for fixed periods of time.

EXPERIMENTAL

Materials

The materials used - metals, test liquids and coatings - are described in detail in Appendix I. The metals and liquids were the same as for Task I and the low energy coatings were the fluorocarbon polymers, TE-3170 and FEP Teflon; a fluorocarbon telomer, Vydax 201G; two acrylic or methacrylic acid polymers or copolymers with fluorinated side chains introduced by esterification, Zepel B and TLF-2475; and two low molecular weight compounds, a fluorinated compound containing a phosphoric acid grouping, TLF-1914, and perfluoro-octanoic acid (see Table II).

Application of Coatings

The planchets to be coated were polished and cleaned as for Task I. Then, unless the surfaces were to be chemically modified, the coatings were applied to the freshly cleaned surfaces. The details of the application and baking of the low energy coatings are given in Appendix III. For the polymeric materials, two methods were used, dipping and electrostatic spraying. Each gave rise to a visible coating which, after evaporation of the dispersion medium, could be baked at an elevated temperature to remove low molecular weight constituents, to promote flow out to a continuous film, and to impart adhesion. The baking temperatures (see Appendix III) were in the ranges suggested by the manufacturers but information on the melting behavior obtained from differential scanning calorimetry was also taken into account in choosing the specific temperatures to be used. For the two low molecular weight compounds, the cleaned, polished planchets were coated by the retraction method used by Zisman and his co-workers (6). The retraction was performed either from a solution in decane (for perfluoro-octanoic acid) or Freon 113 (for TLF-1914). With amphipathic molecules such as perfluoro-octanoic acid and TLF-1914, this technique is believed to leave a closely-packed monolayer on the surface.

With but few exceptions, cleaned, polished planchets of each of the three metals were coated with each of the seven coatings. For some metal-coating combinations, additional planchets were prepared under similar or modified conditions, depending on whether the first coating appeared to have had a flaw or whether it was believed that modified conditions (e.g. increased baking temperature) would improve coating performance. In addition, before coating with TLF-1914, some planchets of each metal were oxidized in a plasma, some planchets of copper were sulfided, and some aluminum planchets were anodized. Another special pretreatment which involved the dipping of the polished and cleaned metal planchets in a solution of a silane (γ-aminopropyltriethoxysilane) in m-xylene and then allowing them to air dry was, in some cases, applied before the application of FEP Teflon, Zepel B and TLF-2475. Following the silane treatment, the coating material had to be sprayed on since the silane prevented uniform transfer of the coating material to the surface by dipping.

Contact Angle Measurements

The contact angle goniometer used in Task I was also used in Task II, but the measurements were made with the samples mounted in a thermostatted glass cell rather than in the environmental chamber. Each coated planchet to be tested was placed horizontally on a support in the cell and small drops of the chosen test liquid were placed on the surface using a hypodermic syringe fitted with a 0.02 cm i.d. (26-gauge) needle or, for Freon 11, a narrow bore Teflon tube. In the case of measurements with water and methanol, the cell was held at 20° ± 0.5°C but for Freon 11, because of its high rate of evaporation at 20°C, the cell temperature was 18° ± 0.5°C. While contact angle measurements were generally made with the goniometer, some measurements with Freon 11 were made from photographs using a protractor. This was because the rapid evaporation of Freon 11 made measurements with the goniometer difficult. Whereas replicate measurements of a single angle with the goniometer normally had a standard deviation of about 0.8°, measurements with Freon 11 had higher errors due to the increased difficulties arising from the high rate of evaporation. It was estimated that these errors were probably about twice as large as for the other liquids, but this could not be established directly since replicate measurements could not be made on a single drop.

Durability Studies

The durability studies of Task II were intended to give a rapid indication of the relative durabilities of the coatings under the most drastic conditions that might be encountered in a heat pipe - continuous immersion in the test liquid at the boiling point. Contact angles of the test liquids on the coated planchets were determined before and after 24 and/or 48 hour periods of immersion in the liquids. Changes in the contact angles were considered as possible indications of coating deterioration. To avoid cross-contamination and scratching of the coated surfaces, each planchet exposed to a refluxing test liquid was held in a separate test tube.

RESULTS

The results of Task II are summarized in Tables V, VI and VII. Table V gives the data for water, Table VI for methanol and Table VII for Freon 11.

Water

The tabulated results for water (Table V) show the following:

1. With but one exception, the as-prepared, coated surfaces all gave contact angles in the 107° to 121° range. The exception was the FEP Teflon sprayed on to a previously-applied silane coating; this gave a contact angle of 102°.

2. The exposure to boiling water for 24 or 48 hours always produced a reduction in contact angle. The range of the reduction was from about 2° to about 100°. The largest reductions occurred for aluminum planchets because of corrosion and for planchets coated with TLF-1914 which may have dissolved in the water.

3. Except for effects clearly due to corrosion of aluminum, the coatings appeared to behave similarly on each of the three metals.

4. The dipped coatings of TE-3170 performed better than the electrostatically sprayed coatings. Also the sprayed coating of FEP Teflon on a previously applied coating of silane performed less well than dipped coatings applied directly to the substrate.

5. None of the TLF-1914 coatings withstood immersion in boiling water.

6. Judging from the magnitudes of the reductions in contact angle for the dipped or retracted coatings, the order of decreasing durability for the coatings appears to be:

TE-3170 and FEP Teflon > Vydax 201G > TLF-2475 and Zepel B > TLF-1914

7. The silane pretreatment was possibly beneficial for the TLF-2475 but it did not appear to be for FEP Teflon or Zepel B.

8. Immersion in boiling water usually resulted in increased standard deviations for the measured contact angles.

TABLE V

CONTACT ANGLES (degrees) OF WATER ON COATED METAL SURFACES IN AIR AT 20°C
BEFORE AND AFTER EXPOSURE TO BOILING WATER

Coating Material	Coating Conditions			Metal Substrate and Exposure Time (hours)								
				Stainless Steel			Copper			Aluminum		
	M	T	t	0	24	48	0	24	48	0	24	48
TE-3170	S	350	30	115±1	108±1	106±3	108±3	99±7	(a)	111±3	110±2	(a)
TE-3170	D	350	30				117±1	-----	114±2	117±1	-----	115±1
Vydax 201G	S	350	30	114±1	111±2	101±2	114±1	107±3	103±1	114±1	110±1	(a)
Vydax 201G	S	350	30	112±4	-----	103±2						
Teflon FEP	D	320	30				115±1	-----	110±1	115±1	-----	102±5
Teflon FEP	D	280	30	111±2	108±1	108±3						
Teflon FEP-Silane	S	330	30	102±1	-----	83±4				111±1	-----	(a)
Zepel B	D	190	30				120±1	-----	100±9	120±1	-----	(a)
Zepel B	D	180	30	119±1	101±7	-----						
Zepel B	S	240	30	115±2	102±4	-----						
Zepel B-Silane	S	210	30	118±1	-----	94±4				121±1	-----	(a)
TLF-2475	D	180	30	116±1	93±8	-----						
TLF-2475	D	190	30				120±1	-----	111±1			
TLF-2475	S	240	30	114±3	98±4	-----						
TLF-2475-Silane	S	210	30	120±1	-----	117±1				120±1	-----	(a)
TLF-1914	R	---	--	113±2	-----	<20	118±2	-----	(a)			
TLF-1914-oxide	R	---	--				111±5	-----	(a)	112±2	-----	(a)
TLF-1914-sulfide	R	---	--				118±2	-----	(a)			
TLF-1914-anodized	R	---	--							107±4	-----	(a)
None	-	---	--	0	-----	-----	0	-----	-----	0	-----	-----

a - Corrosion of surface.

M - Method of coating: D = Dip, S = Spray, R = Retraction

T - Baking temperature (°C).

t - Baking time (minutes).

Methanol

The results for methanol (Table VI) show some similarities and some differences from those for water. The main points to be noted are:

1. The range of contact angles on the as-prepared, coated surfaces, except for very low values below 25° for perfluoro-octanoic acid, was 41° to 73°.

2. The immersion in methanol at the boiling point produced a large reduction in the contact angle, 20° or more, on coatings of Zepel B, TLF-2475 and TLF-1914, but only a small reduction, less than 5°, on coatings of TE-3170, FEP Teflon and Vydax 201G.

3. There was no obvious corrosion of the aluminum alloy by boiling methanol. The coatings behaved similarly on all three metals.

4. None of the TLF-1914 coatings appeared capable of withstanding exposure to boiling methanol.

5. The order of decreasing durability for the coatings appeared to be:

   TE-3170, FEP Teflon and Vydax 201G > TLF-2475 > Zepel B > TLF-1914.

6. The silane pretreatment may have been beneficial for TLF-2475 but it was not for FEP Teflon or Zepel B.

7. Immersion in boiling methanol frequently resulted in an increased standard deviation in the contact angles.

Freon 11

The results for Freon 11 (Table VII) show the following features:

1. The range of contact angles on the as-prepared, coated surfaces was from about 3° to 40°.

TABLE VI

CONTACT ANGLES (degrees) OF METHANOL ON COATED METAL SURFACES IN AIR AT 20°C BEFORE AND AFTER EXPOSURE TO BOILING METHANOL

Coating Material	Coating Conditions			Metal Substrate and Exposure Time (hours)								
				Stainless Steel			Copper			Aluminum		
	M	T	t	0	24	48	0	24	48	0	24	48
TE-3170	D	350	30	51±1	50±1	50±1	51±1	49±1	48±3	52±1	49±1	49±1
Teflon FEP	D	280	30	52±1	52±1	52±1	53±1	53±1	51±1	53±1	50±1	49±1
Teflon FEP-Silane	S	330	30				43±4	40±3	38±4			
Vydax 201G	S	350	30	41±1	----	----	41±1	44±1	41±2	41±1	39±2	40±1
Zepel B	D	180	30	71±1	46±8	42±4	72±1	52±2	45±4	73±1	44±5	42±4
Zepel B	D	190	30	71±1	40±6	34±1	71±1	38±5	----	71±1	39±7	40±1
Zepel B-Silane	S	210	30				59±2	44±1	39±2			
TLF-2475	D	180	30	69±2	48±14	----	70±1	42±9	51±2			
TLF-2475	D	190	30	70±1	54±1	----				67±1	----	48±2
TLF-2475-Silane	S	210	30				72±1	49±2	51±2			
TLF-1914	R	---	--	52±1	----	22±3	53±1	----	0	54±1	----	15±1
TLF-1914-oxide	R	---	--	54±1	----	0	55±1	----	0	56±1	----	13±4
TLF-1914-sulfide	R	---	--				55±1	----	0			
TLF-1914-anodized	R	---	--							46±1	----	0
Perfluoro-octanoic Acid	R	---	--	13	----	----				23±1	----	----
None	-	---	--	0	----	----	0	----	----	0	----	----

M - Method of coating: D = Dip, S = Spray, R = Retraction

T - Baking temperature (°C).

t - Baking time (minutes).

TABLE VII

CONTACT ANGLES (degrees) OF FREON 11 ON COATED METAL SURFACES IN AIR AT 18°C
BEFORE AND AFTER EXPOSURE TO BOILING FREON 11

Coating Material	Coating Conditions			Metal Substrate and Exposure Time (hours)								
				Stainless Steel			Copper			Aluminum		
	M	T	t	0	24	48	0	24	48	0	24	48
TE-3170	D	350	30	7±1	----	7±1	8±1	----	7±1	7±1	----	8±1
TE-3170	S	350	30	<3	----	----						
Vydax 201G	S	350	30	<3	----	----						
Teflon FEP	D	280	30	9±1	10±1	9±1	8±1	9±1	10±1	8±1	11±1	11±1
Zepel B	D	180	30	23±1[a]	18±2[a]	16±1[a]	24±1	29±1	28±1	25±1	25±1	24±2
Zepel B	D	190	30	30±2	----	17±2				30±2	----	22±2
TLF-2475	D	180	30				24±1	27±2	27±2	23±1	14±5	18±5
TLF-2475	D	190	30	19±2	----	12±2	21±2	----	12±1			
TLF-1914	D	24	60	33±2	----	30±1	24±1	----	12±2	40±1	----	30±1
TLF-1914-oxide	R	---	--	40±1	----	31±1	25±1	----	12±2	40±1	----	31±1
TLF-1914-Sulfide	R	---	--				25±2	----	18±2			
TLF-1914-anodized	R	---	--							28±2	----	28±1
Perfluoro-octanoic Acid-oxide	R	---	--	20±2	5±1	----				20±2	6±1	----
None	-	---	--	0	----	----	0	----	----	0	----	----

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a. Coating baked in air for additional 5 minutes at 320°C.

M - Method of coating: D = Dip, S = Spray, R = Retraction.

T - Baking temperature (°C).

t - Baking time (minutes).

2. The immersion in Freon 11 at the boiling point sometimes produced a decrease in contact angle but there were several cases in which a small increase in contact angle was observed.

3. The coatings tended to behave similarly on the three metals but with a marked exception that the as-prepared coated surfaces with TLF-1914 gave lower contact angles with copper substrates than with stainless steel or aluminum alloy.

4. While dipped coatings of TE-3170 and FEP Teflon appeared to be durable to boiling Freon 11, the contact angles upon them were only about 9°.

5. The systems with contact angles above 20° which showed the best promise of durability were Zepel B on copper, Zepel B on aluminum alloy, TLF-2475 on copper, TLF-1914 on stainless steel and TLF-1914 on anodized aluminum alloy.

Some possible explanations of the results with the three liquids will be put forward in the Discussion Section at the end of this report.

CONCLUSIONS (TASK II)

On the basis of the results in Tables V and VI, it was concluded that, of the coatings investigated, two performed well with water and methanol both from the points of view of high contact angle and contact angle stability. These were the fluorocarbon polymer coatings, TE-3170 and FEP Teflon, applied by dipping. The fluorocarbon telomer, Vydax 201G, which was applied by spraying, was not as good but it did show stability of contact angle with methanol, though the angle was about 10° lower than for the fluorocarbon polymers - about 41° as against 51°. No other coatings performed as well with water and/or methanol on all three metals as the three fluorocarbon materials. However, the specific metal-coating system, TLF-2475 on silane-treated stainless steel, gave a high contact angle with water and the contact angle stability appeared good.

No coating which gave both high contact angle and good contact angle stability with Freon 11 was found (see Table VII). The best of those investigated were Zepel B, TLF-2475 and TLF-1914.

TASK III - COATING STABILITY AND CONTACT ANGLE STUDIES IN THE ENVIRONMENTAL CHAMBER

From the range of metal-coating-liquid systems studied in Task II, nine were selected for further study in Task III. They were:

Metal	Coating	Liquid
Stainless steel	FEP Teflon	Water
Aluminum	FEP Teflon	Water
Copper	FEP Teflon	Water
Stainless steel	TE-3170	Water
Stainless steel	TLF-2475-Silane	Water
Stainless steel	FEP Teflon	Methanol
Stainless steel	TE-3170	Methanol
Stainless steel	Vydax 201G	Methanol
Copper	Zepel B	Freon 11

The selection was based on the potential value of the systems for use in heat pipes and it was weighted in favor of water as the working liquid, stainless steel as a structural material, and FEP Teflon and TE-3170 as coatings because of their good performance in Task II.

The objectives of Task III were:

1. to determine, for each system, the solid-liquid-vapor contact angles at 20°C and at the normal boiling point of the liquid in the presence of only the saturated vapor of the liquid.

2. to evaluate the stability of the coatings in terms of the stability of the contact angles.

EXPERIMENTAL

Coated Metal Specimens

For each metal-coating combination, three planchets were prepared. The materials and techniques used were as for Task II.

Contact Angle Measurements

The contact angle measurements were made with the environmental chamber and contact angle goniometer described for Task I. Three identical planchets were used in the chamber in each run. The number of drops measured on each planchet for each set of readings varied but was usually more than three.

At the end of Task III, as a check for contamination in the chamber, a final set of water contact angle measurements as for Task I was carried out on cleaned, polished stainless steel planchets.

Durability Measurements

The durability of each coating was assessed in terms of the variation in contact angle at the normal boiling point when the coated planchets were held in the saturated vapor at the boiling point for at least 18 hours with some liquid present on the planchet surfaces.

RESULTS

The results for Task III are recorded in Tables VIII, IX and X. Table VIII presents the data for the five metal-coating combinations tested with water, Table IX for the three tested with methanol, and Table X for the one with Freon 11. In each case, the results for the three planchets are shown separately. Since the intervals between sets of measurements for each system were not always the same, the intervals between the sets are indicated in the Tables. As an example of the primary measurements in a set, some raw data for copper are given in Table XI.

Water (Table VIII)

1. The behavior of water was similar on the FEP Teflon coatings on each of the three metals. The mean contact angles for each of the three planchets for each metal were all in the range 114° to 116° at both 20°C and 100°C. The 20°C values agree well with the Task II value of 115° for both copper and aluminum (Table V), but less well with the 111° value for stainless steel. There was no significant temperature coefficient of the contact angle and there was no indication of a change in contact angle with

time at 100°C. The coatings on each planchet appeared to be uniform and, further, the planchet-to-planchet variation for the three planchets of each metal was small.

2. The contact angles for water on the TE-3170-coated stainless steel were slightly higher than for water on the FEP Teflon coatings. Each set gave an average of 117°. The results show no evidence of change of contact angle with time, no evidence of non-uniform coating, and no evidence of a non-zero temperature coefficient of the contact angle. The 117° value is the same as that observed for water on the dipped TE-3170 coatings on copper and aluminum in Task II.

3. The contact angles for water on the silane-treated stainless steel with a sprayed TLF-2475 coating were more variable than for the four metal-coating combinations already mentioned. The results show that there is a reduction in contact angle with time at 100°C. They also suggest that there is a small negative temperature coefficient of the contact angle. Further, the increased standard deviations of the contact angles show that the changes which took place at 100°C increased the variability of the coated surfaces, at least for some period of time, though the variability from point-to-point on a planchet, and from planchet to planchet, seemed to disappear on cooling to 24°C. However, a decrease in contact angle seemed to have occurred since the first measurements at 20°C had been made. The initial contact angles at 20°C of 118°-119° were similar to, but a little smaller than, the Task II values of 120° for TLF-2475 on both silane-treated stainless steel and silane-treated aluminum.

4. Overall, the results suggest that both TE-3170 and FEP Teflon can form durable coatings which give high water contact angles. However, the variations of water contact angle with time and temperature on TLF-2475-coated, silane-treated, stainless steel raise doubts about the stability of this metal-coating combination.

Methanol (Table IX)

1. The methanol contact angle results for FEP Teflon and TE-3170 coatings on stainless steel are similar. Both show contact angles which do

TABLE VIII

CONTACT ANGLES (degrees) OF WATER ON COATED METAL SURFACES IN A SATURATED VAPOR ATMOSPHERE

Stage Temp.	20°C		100°C			24°C
Set No.	A	B	C	D	E	F

a. Water on 301 Stainless Steel dip coated with Teflon FEP

Interval[a] (hrs.)	-	6	22	6	14	---
	116[b](12)[c]	115(32)	116(16)	116(10)	115(6)[d]	---
	115(12)	115(30)	115(16)	115(10)	115(6)[d]	---
	115(14)	115(30)	116(16)	115(10)	116(8)[d]	---

b. Water on ASTM B-88-61 Copper dip coated with Teflon FEP

Interval (hrs.)	-	-	6	14	24	---
	114(22)	---	116(18)	116(12)	115(10)	---
	114(16)	---	115(20)	116(18)	115(20)	---
	115(20)	---	115(14)	115(16)	115(20)	---

c. Water on 6061-T6 Aluminum dip coated with Teflon FEP

Interval (hrs.)	-	-	5	14	4	---
	116(16)	---	116(18)	116(18)	---	---
	116(18)	---	116(18)	116(18)	116(8)	---
	116(16)	---	116(18)	116(18)	---	---

d. Water on 301 Stainless Steel dip coated with TE-3170

Interval (hrs.)	-	-	4	18	2	---
	117(20)	---	117(22)	117(22)	117(12)	---
	117(22)	---	117(24)	117(22)	117(12)	---
	117(24)	---	117(24)	117(22)	117(12)	---

e. Water on silane-treated 301 Stainless Steel spray coated with TLF-2475

Interval (hrs.)	-	-	22	18	-	67
	119(42)	---	116(22)	112±4(24)	---	116(12)
	118(48)	---	115±2(24)	112±3(20)	---	116(12)
	118(56)	---	117(22)	116(22)	---	116(12)

---

a. Interval since previous set.

b. Standard deviation is about ± 1° unless noted otherwise.

c. Numbers in parentheses are number of measurements averaged.

d. Temperature was 96°C.

not change significantly either with time or with temperature. The contact angles on FEP Teflon are about 51° at both 20°C and 64.7°C while for TE-3170 they are about 52° at both temperatures. The Task II values were similar with 52° for FEP Teflon and 51° for TE-3170.

2. Vydax 201G on aluminum gave lower methanol contact angles than the TE-3170 and FEP Teflon on stainless steel. The values were about 40° at 20°C and 41° at 64.7°C which agreed well with the 41° value of Task II. There is some evidence of a small negative temperature coefficient of contact angle; however, no change in contact angle with time was observed at 64.7°C.

3. TE-3170, FEP Teflon and Vydax 201G all appeared to give stable methanol contact angles.

Freon 11 (Table X)

1. The contact angles of Freon 11 on Zepel B-coated copper were much more variable than the contact angles for the other systems which have been discussed. In this case, the variation seemed to be associated with the presence or absence of small drops of condensate on the planchet surfaces. If, as for the measurements recorded in columns A, C and D of Table X, the condensate was not visible, the contact angles were in the 30° to 37° range. On the other hand if, as for B and E, the condensate could be seen, the contact angles were in the 21° to 27° range. The data is insufficient to show whether there was a change in contact angle with time but observation of the planchet surfaces at the end of the run suggested that the coatings had been altered where large drops had been in contact with them.

2. The data suggests that there must be a doubt about the stability to Freon 11 of Zepel B coatings.

Check for Contamination of the Environmental Chamber

The results of the final set of contact angle measurements, for water on cleaned, polished, uncoated stainless steel, are given in Table XII. Comparison with the data in the last column of Table IV shows that the chamber had remained essentially free from low energy surface contaminants during Task III.

TABLE IX

CONTACT ANGLES (degrees) OF METHANOL ON COATED METAL SURFACES IN A SATURATED VAPOR ATMOSPHERE

Stage temp.	20°C	64.7°C			
Set No.	A	B	C	D	E
a. Methanol on 301 Stainless Steel dip coated with Teflon FEP					
Interval[a] (hrs)	-	19	6	14	1
	51[b](16)[c]	51(10)	52(10)	50-51(2)	51(8)
	51(16)	51(14)	52(6)	50-51(2)	52(6)
	51(16)	52(16)	51(8)	51(6)	51(8)
b. Methanol on 301 Stainless Steel dip coated with TE-3170					
Interval (hrs)	-	4	18	-	2.5
	52(18)	53(18)	52(16)	-------	52(12)
	52(18)	52(18)	52(18)	-------	52(12)
	52(20)	52(20)	53(16)	-------	53±2(12)
c. Methanol on 6061-T6 Aluminum spray coated with Vydax 201G					
Interval (hrs)	-	5	18	-	1.5
	40(14)	40(18)	40(18)	-------	d
	40(18)	41(20)	41(18)	-------	41(8)
	39(18)	42(18)	41(18)	-------	41(8)

---

a. Interval since previous set.

b. Standard deviation is about ±1° unless noted otherwise.

c. Numbers in parentheses are number of measurements averaged.

d. Surface was contaminated by specks of corrosion products from the brass syringe mounting.

TABLE X

CONTACT ANGLES (degrees) OF FREON 11 ON ASTM-B-88-61 COPPER DIP COATED WITH ZEPEL B IN A SATURATED VAPOR ATMOSPHERE

Stage temp.	20°C	23.8°C			
Set No.	A	B	C	D	E
Interval[a] (hrs)	-	18	1	27	1
	30±2(24)[b]	22±2(16)[c]	-------	36±3(20)	27±1(10)[c]
	32±3(12)	21±2(16)[c]	36±2(6)	34±3(22)	26±1(10)[c]
	35±6(18)	22±2(10)[c]	-------	37±2(20)	24±1(10)[c]

---

[a] Interval since previous set.

[b] Numbers in parentheses are number of measurements averaged.

[c] Surfaces had small droplets of condensate upon them when measurements were made.

CONCLUSIONS (TASK III)

The results of Task III showed that seven of the nine systems selected for study in the environmental chamber gave stable contact angles at the boiling points of their respective liquids. They also showed that, for the seven systems, the contact angles measured at 20°C in the chamber in the absence of air were similar to those measured in air in Task II. The two systems about which there is some doubt are:

Stainless steel - TLF-2475/Silane - Water
Copper - Zepel B - Freon 11.

The doubts concern unexplained changes in contact angles with time which may indicate deterioration of the coatings.

The seven systems which showed stable contact angles at the boiling points of the liquids were:

Metal	Coating	Liquid
Stainless steel	FEP Teflon	Water
Copper	FEP Teflon	Water
Aluminum	FEP Teflon	Water
Stainless steel	TE-3170	Water
Stainless steel	FEP Teflon	Methanol
Stainless steel	TE-3170	Methanol
Aluminum	Vydax 201G	Methanol

The results of Tasks I, II and III will be discussed in more detail in the next section.

TABLE XI

RAW DATA FOR THE COPPER - FEP TEFLON - WATER SYSTEM, PLANCHET NO. 43

Set No. Stage Temp. (°C) Time at start Time interval[a] (hrs.)	A 20 12 noon(2/18) -	B 100 6:17pm(2/18) 6	C 100 9:12am(2/19) 14	D 100 10:30am(2/20) 24
Drop No.	Pairs of Goniometer Readings (Degrees)			
1	115,116	115,116	115,116	115,116[b]
2	114,115	115,116	116,116	115,115
3	112,113	116,116	114,115	115,116
4	112,113	113,114	115,116	114,116
5	112,113	114,115	115,116	115,115
6	113,114	115,116	115,116	
7	115,115	115,116	116,115	
8	115,115		115,115	
9	114,115			
10	114,114			

a. Interval since previous set.

b. Readings in set D are for a single drop of increasing size.

TABLE XII

FINAL CONTACT ANGLES (degrees) OF WATER ON CLEANED, POLISHED STAINLESS STEEL IN THE PRESENCE OF PURE VAPOR AT 20°C AND 100°C

Stage Temperature	20°C		100°C	
Time Interval (hrs.)	-	20	5	20
Planchet No. 70	11±2(14)[a]	12±2(12)	13±1(12)	24±1(12)
Planchet No. 71	11±3(14)	11±1(12)	14±2(12)	25±2(12)

a. Figure in parentheses is number of measurements averaged.

DISCUSSION AND CONCLUSIONS

The experimental results of Tasks I, II and III have been given in the previous sections. In this section, the results will be discussed and some possible explanations of the observed effects will be put forward.

The contact angles of each of the three liquids on the freshly cleaned metals were essentially zero (see Tables V, VI and VII). However, the cleaned metals quickly became contaminated in air, or in the carefully cleaned environmental chamber (Tables IV and XII). These results are in general accord with the findings of others. Thus, Fox, Hare and Zisman (15) have concluded that all pure liquids, other than certain autophobic liquids, spread spontaneously on all clean high energy surfaces, including metals. Also, Bewig and Zisman (13) and Trevoy and Johnson (12), among others, have pointed out that prolonged exposure of a clean metal or other hydrophilic surface to any atmosphere other than a most carefully purified gas can result in water contact angles from a few degrees to 90°. While the non-zero water contact angles (Tables IV and XII) obtained on the cleaned metals in the environmental chamber must have indicated contamination, the contact angles were sufficiently low to show that the contamination was unlikely to have affected the results for the coated metals.

The highest initial contact angles of water (121°, see Table V) and methanol (73°, see Table VI) on as-prepared coatings were obtained with the acrylate-type polymers with fluorinated side chains, Zepel B and TLF-2475. TLF-1914 also gave a high initial value (118°) with water. Each of these coatings is believed to provide a CF_3-rich surface.

The largest contact angle for water observed by Shafrin and Zisman (3) was 120°. This was for the CF_3-rich surface of a polymethacrylic ester with perfluorinated side chains which was probably chemically similar to Zepel B and TLF-2475. Thus, the present results for water appear to be in agreement with those of Shafrin and Zisman.

Almost all the systems showed a drop in contact angle following immersion in any of the three test liquids at the boiling point (Tables V, VI and VII). In some cases, the drop was a large fraction of the initial contact angle, in others it was only small, and in rare cases a small increase in contact angle was observed. For coated aluminum planchets exposed to water (Table V), corrosion of the metal must be considered to have been the major cause of the changes in contact angle. For TLF-1914, and perfluorooctanoic acid coatings of the monolayer type, penetration by, or solution in, the liquid seem possible causes of the generally large drops in contact angle with all three liquids (Tables V, VI and VII).

The polymeric coatings could be divided into two categories by their behavior: Zepel B and TLF-2475, which generally gave high initial contact angles which subsequently fell substantially; and TE-3170, FEP Teflon and Vydax 201G which gave more stable contact angles. As has been pointed out by Adam (16), reduction of contact angle as a result of exposure of a solid to a liquid is a common phenomenon. In the case of a coating, it does not necessarily indicate lack of durability. However, if the contact angle of a liquid on a low energy coating continues to decrease toward the value for the underlying solid, or if a previously uniform surface starts to show variations from point to point, then this almost certainly indicates loss of uniformity and, probably, deterioration. Adam considers the usual cause of a reduction in contact angle during exposure of a solid to a liquid to be the soaking of the liquid into the solid.

The drop in the water and methanol contact angles of Zepel B and TLF-2475 (Tables V and VI) upon immersion in the boiling liquids could have been due to chemical changes in the coatings. In the case of methanol, transesterification resulting in the replacement of perfluorinated groups by methyl groups must be considered a possibility and, with water, hydrolysis of the ester groups. Another possible explanation of the reduced contact angles is reorientation of polar groups in the coating in the presence of the polar liquids; such effects have been mentioned by Rideal (17) and by Langmuir (18). However, at least in the case of methanol, transesterification seems more likely since remeasurement of methanol contact angles on the

Zepel B and TLF-2475 coated planchets after storage in the air for about one month showed no changes from the 48 hour values of Table V. Other possible causes such as "soaking in" of liquid or reorientation would be expected to be reversible.

The coatings with the most stable contact angles, at least to water and methanol, were the fluorocarbon materials TE-3170, FEP Teflon and Vydax 201G. Their initial water contact angles were in the 108° to 117° range (Table V).

Shafrin and Zisman (3) have stated that no water contact angle lower than 108° is found for any homo- or copolymer exposing C and F atoms only. Thus, the initial contact angles observed in the present study were in the expected range, though the values measured after exposure to boiling water were sometimes lower than 108°. The higher contact angle stability of the fluorocarbon materials as compared with the acrylic polymers, Zepel B and TLF-2475, is probably due to the structural uniformity of the fluorocarbon molecules and their freedom from reactive polar groups.

TLF-1914 coatings gave the highest initial contact angles (40°) with Freon 11 (Table VII). The contact angles generally fell as a result of immersion in the boiling liquid but, after 48 hours, certain of the TLF-1914 coatings still had higher Freon 11 contact angles than were shown by the other materials. Some Zepel B and TLF-2475-coated planchets also showed ability to withstand immersion in boiling Freon 11 without a major reduction in contact angle.

As mentioned in the Introduction, calculations based on Fowkes' theory (10) suggest that the highest contact angle to be expected for Freon 11 on any surface is about 45°. Thus, the initial 40° value for the TLF-1914 coated planchets appears to approach to within a few degrees of the calculated maximum. The reduction in contact angle due to immersion in boiling Freon 11 could have been due to solution of the TLF-1914 coating in the liquid though, among other possibilities, corrosion of the metal surfaces by halogen decomposition products of Freon 11, and solution of Freon 11 in the coating, cannot be ruled out. In the cases of Zepel B and TLF-2475, there is some evidence of increased contact angles following the immersion in boiling Freon 11. The reason for this is not clear, but it may be pointed out that Neumann, Haage and Renzow (19) have noted an increase of the n-decane contact angle against polytetrafluoroethylene after an exposure of several hours to the liquid.

The low Freon 11 contact angles (<12°) on TE-3170, FEP Teflon and Vydax 201G must be associated with the low concentrations of CF_3 groups in the surface.

At least for water and methanol, and possibly for Freon 11, there is little difference in the initial contact angles measured at 20°C in air at atmospheric pressure or in the absence of air at the vapor pressure of the liquid (compare Tables V and VIII, VI and IX, VII and X). This observation confirms expectation since air is unlikely to have a detectable effect on any of the surface and interfacial tensions which govern the contact angles. These are the liquid-vapor surface tension (γ_{LV}), the solid-vapor surface tension (γ_{SV}), and the solid-liquid interfacial tension (γ_{SL}) (4). The situation would be different if the air were strongly adsorbed on the solid surface or if it dissolved appreciably in the liquid. While few studies to compare contact angles measured in air with those measured in its absence have been made, some measurements by Petke and Ray (20) show that, for water on an FEP fluoropolymer at a high temperature, the air made no difference.

The temperature coefficients of the contact angles of water and methanol on the fluorocarbon coatings TE-3170, FEP Teflon and Vydax 201G studied in the environmental chamber were, within the limites of experimental error, zero. It is possible, though not certain, that water on TLF-2475 had a non-zero temperature coefficient.

Temperature coefficients of contact angles on certain fluorinated surfaces have been recently studied by Petke and Ray (20) and by Neumann, Haage and Renzow (19). Petke and Ray found water on an FEP fluoropolymer to have a temperature coefficient of the advancing contact angle of -0.05 deg/°C between 20° and 80°C while Neumann, Haage and Renzow studied the n-alkanes from decane to hexadecane on polytetrafluoroethylene and found the four highest members to have zero temperature coefficients while decane, undecane and dodecane had temperature coefficients of -0.106, -0.057 and -0.012 deg/°C, respectively. The zero temperature coefficients observed in the present study are in the same range of magnitudes as those of the other workers.

The contact angle stability of the metal-coating-liquid systems generally appeared greater in the Task III measurements than in Task II (compare Tables V and VIII, VI and IX, VII and X). This probably indicates the liquid-vapor environment in the environmental chamber was less aggresive than the environment provided by the boiling liquid.

SUMMARY OF RESULTS

Seven coating materials were evaluated in a study to develop stable low energy surfaces on 301 stainless steel, ASTM B-88-61 copper and 6061-T6 aluminum alloy. The contact angles of interest were those with water, methanol and Freon 11 and coating stability was evaluated in terms of change in contact angle at 20°C after immersion in the boiling liquid for 24 or 48 hours. The coating materials were the fluorocarbon polymers, TE-3170 and FEP Teflon; the fluorocarbon telomer, Vydax 201G; the acrylic acid polymers or copolymers esterified with perfluorinated alcohols, Zepel B and TLF-2475; and the lower molecular weight perfluorinated monolayer-forming compounds, TLF-1914 and perfluoro-octanoic acid.

The initial contact angles on the coatings were essentially independent of the metal substrate. The highest angles (in degrees) for the various coatings with the three liquids can be summarized:

Coating	Water	Methanol	Freon 11
TE-3170	117(115)	52(50)	8(8)
FEP Teflon	115(110)	53(52)	9(11)
Vydax 201G	114(103)	41(41)	<3
Zepel B	121(100)	73(45)	30(28)
TLF-2475	120(117)	72(51)	24(27)
TLF-1914	118(<20)	56(22)	40(31)
Perfluoro-octanoic acid	-------	23	20

The values in parentheses are the highest contact angles observed after a 48 hour exposure to the boiling solvent.

Following screening of a large number of metal-coating-liquid systems, nine systems selected because of particular promise for use in heat pipes were tested in a specially designed and constructed environmental chamber. The chamber made possible the measurement of contact angles in the presence of the saturated vapor of the test liquid as the only vapor phase. Further, measurements could be made at temperatures between 20° and 100°C. For each system tested in the chamber, measurements were made at 20°C and at the normal boiling point of the liquid, the measurements at the boiling point being extended over at least 18 hours in a study of contact angle stability. The chamber was also used to study the contact angles of the three liquids on the three cleaned and polished metals under the same conditions.

The main conclusions drawn from the study were:

1. The contact angles of methanol and Freon 11 on cleaned, polished stainless steel, copper and aluminum at 20°C and at the normal boiling points are 0°. The contact angles of water on the clean metals are probably zero though generally small (ca 20°) variable angles were obtained in the present study probably due to adsorption of organic vapors from the atmosphere.

2. The aluminum was visibly corroded by a few hours exposure to water at 100°C. The corrosion was not always prevented by the applied coatings. The copper also showed signs of corrosion though the volume of corrosion products was much smaller than for aluminum.

3. Immersion of a coated metal in a boiling liquid for 24 or 48 hours nearly always resulted in a decrease in the 20°C contact angle against the liquid. The largest decreases appeared to result from corrosion of aluminum by water or exposure of TLF-1914 or perfluro-octanoic acid-coated metals to the liquids.

4. From the points of view of high and stable contact angle, the best coatings for use with water and methanol were the fluorocarbon polymers TE-3170 and FEP Teflon. Greater reductions of contact angle occurred with Zepel B and TLF-2475. These may have been due to hydrolysis of the ester groups by water or transesterification by methanol.

5. With Freon 11, no coating performed in a clearly superior manner when judged on the basis of high and stable contact angle. The best metal-coating combinations appeared to be Zepel B - copper, Zepel B - aluminum, TLF-2475 - copper, TLF-1914 - stainless steel, and TLF 1914 - anodized aluminum.

6. The contact angles for a given metal-coating-liquid system were similar whether measured in a cell open to the air or in the environmental chamber in the presence of the vapor of the test liquid as the only vapor phase.

7. Seven of the nine metal-coating-liquid systems tested in the environmental chamber appeared to have high contact angles and good contact

angle stability. These were:

Metal	Coating	Liquid	θ(at B.Pt.)
Stainless steel	FEP Teflon	Water	115
Aluminum	FEP Teflon	Water	116
Copper	TEP Teflon	Water	115
Stainless steel	TE-3170	Water	117
Stainless steel	FEP Teflon	Methanol	51
Stainless steel	TE-3170	Methanol	52
Stainless steel	Vydax 201G	Methanol	41

8. Judging from the measurements at 20°C and at the normal boiling points, the temperature coefficients of the contact angles for the seven systems were essentially zero.

9. Changes in contact angle were brought about more rapidly by immersion of coated samples in boiling liquid than by exposure of samples to the saturated vapor and small drops of condensate in the environmental chamber.

10. The contact angles of Freon 11 on Zepel B-coated copper appeared to depend markedly on the presence or absence of condensate on the surface. Thus, without the condensate, contact angles in the 30-37° range were observed whereas when it was visible the angles fell in the 21-27° range. Similar effects were not noted with the eight other systems studied in the environmental chamber. However, no special effort was made to investigate this point.

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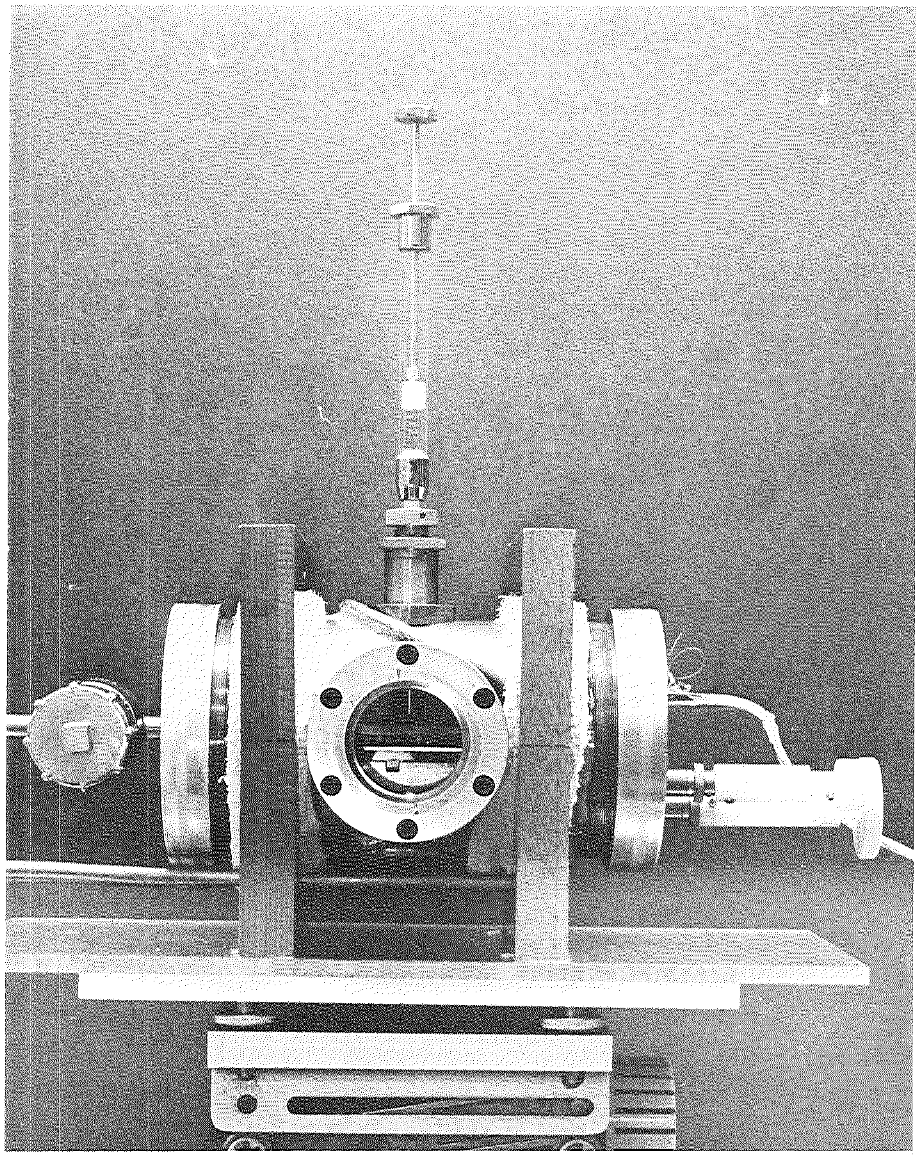

Figure 1. The environmental chamber assembly with insulation removed. The length of the cylindrical chamber is 17 cm. The planchet stage and syringe needle tip can be seen through the window.

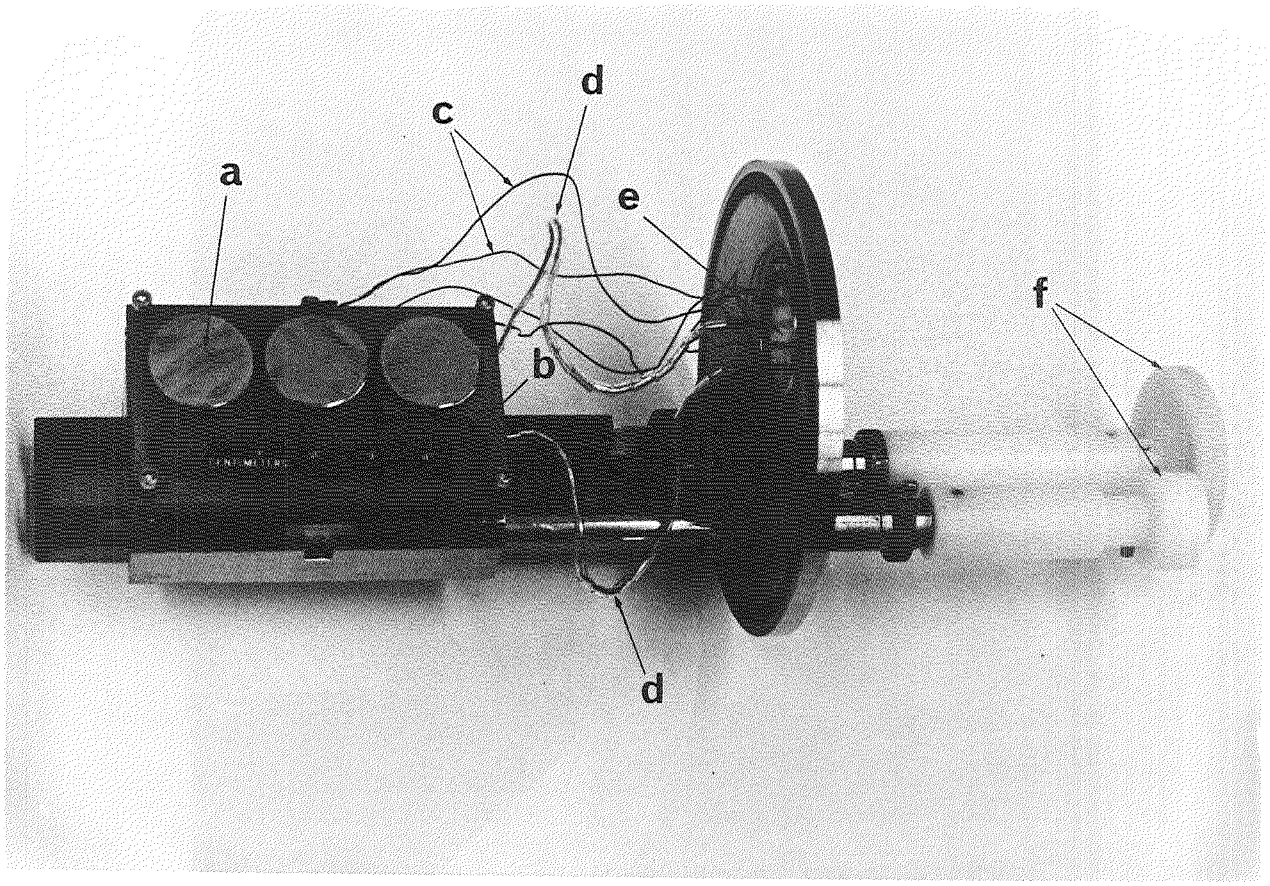

Figure 2. The stage of the environmental chamber. The arrows indicate three planchets (a), the liquid reservoir (b), thermocouple lead wires (c), lead wires for the thermoelectric device (d), the feed-through (e), and the stage control knobs (f).

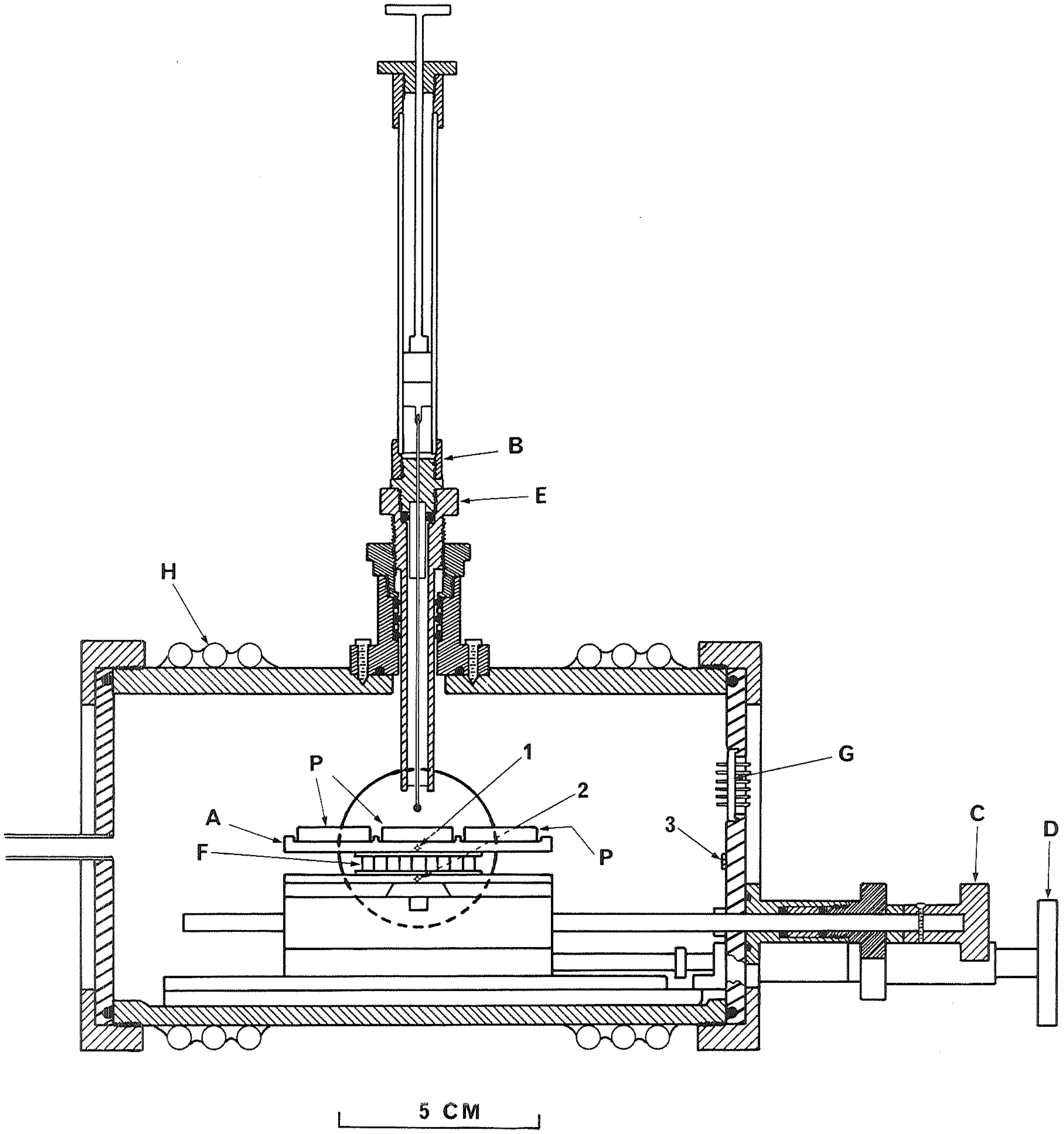

Figure 3. Longitudinal cross-section of the environmental chamber. The parts are described in Appendix II.

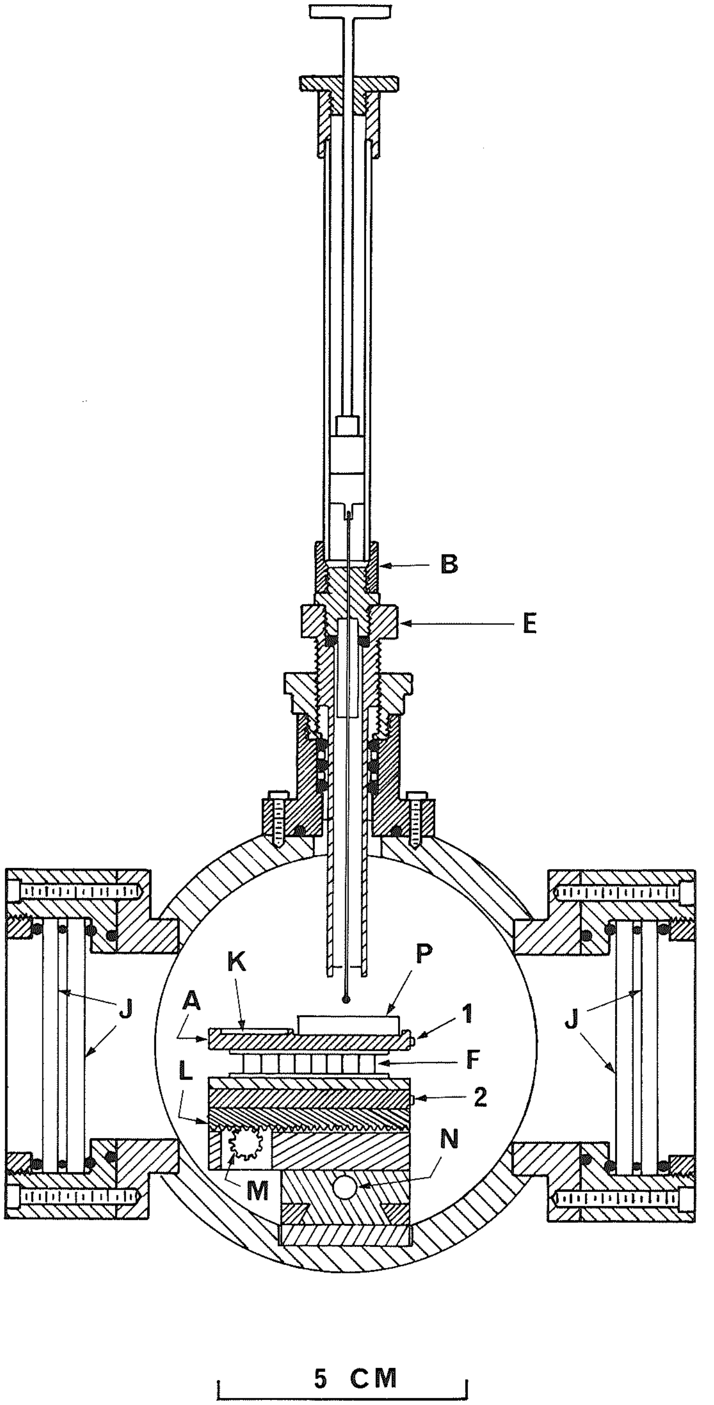

Figure 4. Transverse cross-section of the environmental chamber. The parts are described in Appendix II.

APPENDIX I

Materials and Metal Polishing Procedures

Materials

Metals

The metals used were 301 stainless steel, ASTM B-88-61 copper, and 6061-T6 aluminum alloy. All were obtained from commercial sources.

Liquids

The test liquids were water, methanol, and Freon 11. Spectranalyzed Grade methanol was obtained from the Fisher Scientific Company and 99.8% pure Freon 11 from the du Pont Chemical Company; these were the best grades available commercially. Each liquid was freshly distilled before use. The water was distilled from a potassium permanganate solution in previously distilled and deionized water, the methanol was dried over Linde 5X molecular sieve, and the Freon 11 was distilled in an all glass closed system using dry ice as refrigerant. Chemical and physical properties of the liquids are summarized in Table III.

Coating Materials

Seven coating materials were used. They were the fluorocarbon polymers, TE-3170 and FEP Teflon; the fluorocarbon telomer, Vydax 201G; the polymers or co-polymers of acrylic or methacrylic acid esterified with perfluorinated alcohols, Zepel B and TLF-2475; and the lower molecular weight perfluorinated compounds, TLF-1914 and perfluoro-octanoic acid. The available information about these materials is summarized in Table II. Apart from the perfluoro-octanoic acid which was purchased from K and K Laboratories, all the materials were supplied by the du Pont Chemical Company.

Materials for Pretreatment of Metal Surfaces

Special pretreatments of the metal surfaces required the following compounds: sodium sulfide for the sulfiding of copper, oxalic acid for anodizing the aluminum alloy, and γ-aminopropyltriethoxysilane for silanizing each of the metals. The sodium sulfide and oxalic acid were reagent grade chemicals and the γ-aminopropyltriethoxysilane was Silicone A-1100 from Union Carbide.

Polishing and Cleaning of Metal Planchets

Metal planchets, 1.95 cm diameter, were machined from the metal stock. The copper and aluminum planchets were cut from rods and were 0.63 cm thick, and the stainless steel planchets were cut from plate and were 0.32 cm thick. To obtain smooth, clean metal surfaces with a minimum of contamination by abrasive particles, the following procedure was used:

One face of each planchet was manually ground flat through successive use of #200, #400 and #600 grit silicon carbide paper under flowing tap water. The planchets were then washed in dilute "Tide" detergent solution and scrubbed thoroughly with a camel hair brush to remove embedded abrasive. This was followed by copious rinsing in hot and then cold tap water and, finally, distilled water.

For stainless steel and copper, the rough polishing was done manually using Buehler 5 micron polishing alumina on nylon cloth on a glass back plate. Distilled water was used as the lubricant. Inferior surfaces were obtained if an automatic polishing wheel was used for this step; cold flow patterns were apparent on the surfaces, especially with copper. In addition, microscopic observation showed specimens polished with the polishing wheel contained more embedded abrasives than the manually polished specimens. In the case of aluminum, the rough polishing was done using Buehler "Metadi" diamond paste (6 μm particle size) with "Automet" lapping oil as the lubricant, since aluminum reacts with polishing alumina. The oil was removed by rinsing with iso-propanol followed by vapor degreasing for thirty minutes with trichloroethylene. The degreased planchet was then subjected to the same detergent treatment as the stainless steel and copper specimens.

Final polishing of stainless steel and copper planchets was done manually using Buehler No. 3 gamma alumina (0.05 μm particle size) on Buehler micropore cloth on a glass backing plate with distilled water as lubricant. Magnesium oxide (Buehler "Magomet") slurry in distilled water was used for the final polishing of aluminum. Removal of excess abrasive and embedded particles was accomplished by brushing with a camel hair brush under distilled water followed by gentle brushing on an abrasive-free Micropore cloth under flowing distilled water. The planchets were then allowed to dry in a polyethylene glove box flushed with filtered, ultra-high purity nitrogen.

After polishing, the planchets were vapor degreased with trichloroethylene for thirty minutes in a tall jar provided with a glass coil condenser. To avoid galvanic reaction, only one type of metal planchet was degreased at a time.

The degreased planchets were then immersed in an alkaline bath (Cee-Bee MX-39, 2.9 g/liter) at 60-80°C for twenty minutes. This was followed by copious rinsing with hot tap water, then with hot distilled water and, finally, with cold distilled water. In most cases, the planchets were suspended in the alkaline bath by a Teflon FEP monofilament looped around the circumference. This also provided a holder for the planchet in the water break test (ASTM F21-65) for hydrophobic contamination.

APPENDIX II

The Environmental Chamber

The environmental chamber was used for the measurement of contact angles of liquids on coated metal surfaces in an atmosphere consisting entirely of the saturated vapor of the liquid. It was constructed in the instrument shop of The Gillette Company Research Institute. Details of the apparatus are shown in the photographs of Figures 1 and 2 and the diagrams of Figures 3 and 4.

The main body of the apparatus was made from a piece of stainless steel tubing, 15.24 cm (6 inches) long, 7.62 cm (3 inches) I.D., and 0.635 cm (1/4 inch) thick. Referring to Figures 3 and 4, flange fittings were arc welded at opposite sides of the tubing to provide attachments for front and back windows J. Each window was made of two 0.318 cm (1/8 inch) flat Pyrex discs, separated by Viton O-rings to provide thermal insulation. Forward and backward motion of the stage A was provided by a specially constructed rack L and pinion M controlled through knob C; lateral motion was provided by a threaded shaft N connected to the control knob D. Packing glands for the control rods were equipped with double Viton O-ring seals and were attached to the right end plate. The stage had three circular depressions for holding the planchets P and a shallow trough K which served as a reservoir for holding liquid to ensure a saturated vapor environment.

Liquid was introduced into the chamber through a small bore (0.012 cm I.D., 31 gauge) hypodermic needle and a 2 ml Pressure Lok gas tight syringe (manufactured by Precision Sampling Corporation). Control knob E provided vertical motion of the needle assembly and allowed a pendant liquid drop to be placed on the planchet surface. Knob B controlled the flow of liquid through the needle; screwing it all the way down opened fully the miniature valve of the syringe. The valve was closed by unscrewing knob B 2-1/2 turns.

The main heat input for controlling the temperature of the chamber was provided by thermostatted liquid pumped through the copper coils H soldered around the main cell body. In addition, a thermoelectric device F was installed below the planchet stage, so that the stage temperature could be controlled independently to bring it below that of even the coldest spots on the chamber walls. This was necessary to prevent evaporation of the liquid droplets placed on planchets for contact angle measurements at elevated temperatures. The thermoelectric device was controlled by the rectified output from an autotransformer. Three copper-constantan thermocouple junctions, 1, 2, and 3, were provided for temperature measurements inside the chamber. A reference junction which could be immersed in a constant temperature bath was outside the chamber. Electrical connections to the junctions and the thermoelectric device were made through a six-lead, ceramic-metal seal G, silver-soldered to the end plate carrying the control rods. An all-metal, bellows-sealed, high vacuum valve was silver-soldered to the other end plate for connection to a vacuum manifold.

Prior to assembly of the environmental chamber, the metal components were washed with acetone in an ultrasonic bath and subsequently vapor degreased with trichloroethylene for at least three hours. Also, the Viton O-rings and the Teflon-insulated thermocouple wires were baked in a vacuum oven at 180°C for 6 hours.

The environmental chamber was supported in a cradle of Bakelite-linen laminate (Figure 1). When in use, the chamber and the supports were enclosed in a Plexiglas box insulated with urethane foam. To minimize heat losses, only plastic parts of the control knobs and plastic extensions to syringe controls were allowed to stick out of the box. In addition, small auxilliary heaters were placed within the insulation near the end plates and the front and back windows, and a heating tape was wrapped around the valve, to eliminate cold spots in these areas. The entire assembly was mounted on the optical bench of a contact angle goniometer in a Class 10,000 laminar flow hood to minimize particulate contamination when the cell was opened.

The chamber could be evacuated through a cold trap to a manifold carrying a McLeod gauge. The manifold could be closed off from the pump when it was desired to measure pressures of non-condensable gases in the system, as in tests of leak rate.

For temperature measurements using the thermocouples, the thermocouple output was determined using a galvanometer of known sensitivity. Then, from the known thermoelectric e.m.f. for the couple, the temperature difference from the reference junction attached to the bulb of a mercury-in-glass thermometer in a constant temperature bath was calculated and added to the thermometer reading. Selection between the three junctions in the chamber could be made using a low thermal e.m.f. thermocouple switch.

APPENDIX III

Application of Coatings

Three methods of application of low energy coatings to metal surfaces were employed (a) electrostatic spraying (b) dip coating and (c) retraction from a solution or melt so as to obtain a monolayer. Unless otherwise stated, the metals were polished and cleaned as described in Appendix I.

Electrostatic Spraying

In electrostatic spraying, the polymer dispersions were atomized from a De Vilbis nebulizer held at about 40,000 volts with respect to the grounded metal planchets. The high energy impact of the particles on the metal surface is believed to help vaporize the dispersing solvent and to enhance adhesion of the polymer material to the metal substrate when subsequently baked. Although the method deposited particles of coating material on the surface in a quite uniform distribution, the baked top coats were not generally smooth, probably due to the high melt viscosities of the fluorocarbon polymers used. Thus, it is difficult to obtain a smooth, thin, coherent film, especially with large particle size dispersions. However, for Vydax 201G, a low molecular weight Teflon TFE telomer available as a 5 micron average particle size dispersion in a non-aqueous medium, electrostatic spraying was the only method found suitable for depositing the polymer on the metal substrates. This was because the sedimentation of the large particles and the volatility of the dispersion medium led to non-uniform dipped coatings.

In a typical electrostatic spraying experiment, the dispersion concentration was 0.5% by weight; the power supply was set at 39.5 KV; the atomizer nozzle to planchet distance was 7.5 cm; and the air pressure was 1.36 atmospheres (20 psi) when the atomizer was activated. The nozzle was mounted on an optical bench so that it was constrained to move along a single axis. The procedure was to turn on the power supply, activate the atomizer while the nozzle was not directly in front of the planchet to be coated, and then move the atomizer across the planchet face at a uniform rate. The process could be repeated to give the desired coating thickness.

After application, the coatings were baked in a specially built stainless steel cassette which could be flushed with argon or other inert gas while immersed in a salt bath at the appropriate temperature. Baking times reported in Tables V, VI, and VII, are times following the attainment of the desired temperature as indicated by a thermocouple attached to the cassette. The temperatures were in the ranges suggested by the manufacturer though studies with the Differential Scanning Calorimeter were used to ensure that the chosen temperatures were above the melting points of the materials (see Table II).

In certain cases, a silane coupling agent was used to promote adhesion of the electrostatically sprayed coatings. The silanization procedure was to immerse the clean, polished metal planchets, which had been equilibrated with water vapor in a covered Petri dish containing liquid water for at least one hour, in a 1% solution of γ-aminopropyltriethoxysilane (Union Carbide Silicone A-1100) in m-xylene for 12 minutes. The planchets were rinsed in m-xylene and 95% ethanol and allowed to dry. The silanized surfaces were then electrostatically sprayed with the chosen coating as previously described.

Dip Coating

For aqueous dispersions of TE-3170, Teflon FEP, Zepel B and TLF-2475, thinner, more coherent, smoother films were produced by dip coating than by electrostatic spraying. In general, a solids concentration of about 25% was suitable for TE-3170 and Teflon FEP, and about 8% for Zepel B and TLF-2470. These concentrations were obtained by dilution of the stock dispersion with distilled water. A Fisher-Payne Dip Coater was used to pull the cleaned or pretreated planchets up at 5 cm/minute through the surface of the dispersion contained in a 50 ml beaker. For this purpose, the planchets were hung with their plane surfaces vertical using an FEP Teflon monofilament wound around the circumference as a support. Best results were obtained if the planchets were immersed in the dispersion while still wet from cleaning and if the dispersion temperature was in the 50 - 60°C range. If the dispersion was at room temperature, the coatings were thick and uneven due to the drainage pattern of the dispersion. At the higher temperature, rapid evaporation of the dispersion medium from the coated surface took place to leave a uniform coating thin enough to show interference colors. The coatings were baked as for the electrostatically sprayed coatings.

Retraction

In the case of monolayer coatings of TLF-1914 and perfluorooctanoic acid, some of the planchets were subjected to various pretreatments which might improve the bonding. In addition to the coating of cleaned, polished metal surfaces (see Appendix I), monolayer coatings were applied to oxidized surfaces of all three metals, and to sulfided copper surfaces and anodized aluminum surfaces.

The stainless steel and aluminum surfaces were oxidized by exposing the planchets to an oxygen plasma for 5 minutes in a Tracerlab Low Temperature Asher, Model LTA 60; however copper was exposed for only one minute. The sulfide treatment of copper was done by immersing the planchets in 0.1% sodium sulfide solution at room temperature for 5 minutes, and the aluminum planchets were hard anodized in a 3% oxalic acid solution for ten minutes at a current density of 13 ma/cm^2.

The formation of the monolayer coatings was accomplished by immersing the cleaned or pretreated planchets in a saturated solution of perfluorooctanoic acid in n-decane or a saturated solution of TLF-1914 in Freon 113 for at least one hour at room temperature and then slowly retracting them from the solution. This is similar to the procedure described by Zisman et al (14). In most cases, the planchets appeared dry when slowly pulled out of the solution and retained their original appearance. Samples coated by the retraction method were not baked.

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