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Prepared for

National Aeronautics and Space Administration

January 13, 1966

CONTRACT NAS 3-7104

Technical Management
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HARRIS RESEARCH LABORATORIES, INC.
6220 KANSAS AVENUE, N. E. • WASHINGTON, D. C. 20011

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ABSTRACT

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A study was conducted to determine tht effect on contact angles and surface potentials of contaminants applied to clean metal substrates and to determine the effectiveness of currently used propellant tank cleaning procedures in restoring the contact angles and surface potentials to the values obtained on the clean substrates. In addition, contact angle data were obtained for mercury on six different substrates over a range of temperatures from 25 - 150°C.

author

Harris Research Laboratories, Inc.

SUMMARY

This work is part of an overall study of the behavior of liquids in space vehicle tanks under zero gravity conditions. It is essentially a continuation of the work reported in NASA CR-54175 dated December 31, 1964. It consisted of three separate tasks:

1. Clean, flat, polished surfaces of three different structural materials were contaminated in a controlled manner by depositing upon them in thin layers each of seven different typical organic contaminants. The resulting twenty-one contaminated surfaces were then contacted with each of four test liquids, and the advancing and receding contact angles were measured. The structural materials were: Type 301 stainless steel, Type 6061T6 aluminum, and Grade 6 titanium alloy. The contaminants were: graphite, stearic acid, oleic acid, mixed tristearin-triolein, naphthenic oil, paraffin oil, and asphalt. The test liquids were: water, absolute ethanol, unsymmetrical dimethylhydrazine (abbreviated UDMH), and fuming nitric acid, propellant type IIIB (abbreviated IRFNA).

Among the test liquids, water showed the highest contact angles, ranging over 90 degrees (advancing) in most cases. Alcohol and UDMH showed advancing angles as high as 25 degrees on some of the surfaces, but all receding angles and even some of the advancing angles were zero. IRFNA, after a very short induction period during which it presumably reacted with the contaminant, showed zero angles on all the surfaces.

The differences among contaminants with regard to contact angle were relatively small, the exception being graphite which was somewhat more wettable (lower contact angle) than the others.

The underlying substrate had relatively little effect on the contact angle, compared with the dominant effect of the superposed contaminant.

2. The effectiveness of various cleaning procedures used by spacecraft tankage manufacturers was studied by comparing the contact angles of the cleaned surfaces with those of the contaminated surfaces before cleaning. The contact angle measurements were supplemented by measurements of the Volta potential (surface potential) of the contaminated surfaces before and after cleaning. Structural materials and contaminants were the same as used in Task 1 above. Water and absolute ethanol were the test liquids. Cleaning procedures and materials were selected after an extensive survey of current manufacturing practice among contractors for spacecraft and missile tankage. The cleaning materials were also examined in the laboratory, and those which marred the polished surfaces of the uncontaminated metal specimens were eliminated from consideration. Eleven procedures were finally adopted for use in the program; five for stainless steel and three each for aluminum and titanium. Judging from both contact angle and surface potential measurements (which agreed reasonably well with each other) the cleaning procedures varied considerably in their efficacy. Even the poorest of them, however, brought about substantial removal of contaminant, while the best did not bring the surface to its original uncontaminated state.

3. The contact angle of mercury on six different materials was measured as a function of temperature over the range 25-150°C. The materials were Type 347 stainless steel, electrolytic nickel, tungsten, chemical glass (Corning No. 7740), fused quartz, and polytetrafluoroethylene (Teflon, abbreviated PTFE).

The contact angles were very high on all the substrates, ranging at equilibrium from about 130° to 145°. Although there were significant differences between the dynamic advancing and receding angles, equilibrium was rapidly achieved in all systems and the residual hysteresis was negligible. The temperature coefficient of the contact angle was very small in all the systems, and was positive, i.e., the contact angle increased slightly with increasing temperature. The largest increase occurred with PTFE and amounted to about 15 degrees of angle over the 125 degree temperature range explored.

INTRODUCTION

In the weightless environment prevailing in space vehicles the behavior of a liquid is determined largely by its capillary behavior. A controlling parameter of capillary behavior is the contact angle of the liquid against the solid material which forms its container or conduit. Thus, a precise knowledge of the contact angle is necessary in the design of tankage systems for the various liquids used in spacecraft. These include water and an array of propellants. The contact angles of several such liquids against the commonly used structural metals have been previously studied and reported[1] In that study the metals were thoroughly clean and the contact angles were in all cases essentially zero. In actual practice, however, it is difficult to obtain and preserve high cleanliness. The metal surfaces can easily become contaminated by thin localized, easily overlooked layers of the lubricants and other organic auxiliaries used in fabrication. It is therefore a practical necessity to know the effect such layers may have on the contact angles of the important liquids. The first task of the program herein described was to study this effect. The metal substrates chosen were stainless steel, aluminum and titanium. The test liquids were water, absolute ethanol, unsymmetrical dimethylhydrazine (UDMH) and inhibited red fuming nitric acid (IRFNA). The contaminants were selected to represent those likely to be encountered in fabrication. They were stearic acid, oleic acid, mixed tristearin-triolein, naphthenic oil, paraffin oil, asphalt, and graphite. All except the graphite were applied to smooth polished planchets. The graphite had to be applied to satinized planchets to ensure its sticking.

The final procedure in manufacturing spacecraft tankage is a thorough cleaning, intended to remove contaminants. Since this cleaning leaves the metal in its final surface state before actual loading and use, it is important to ascertain its efficacy. The second task of this program was to select a group of cleaning procedures currently being used by manufacturers of this equipment, and see how effectively they removed the contaminants studied under Task 1. This was done by determining the changes in contact angle brought about by the cleaning. In addition to the contact angle studies, the changes in surface potential (Volta potential) were also measured. Surface potential can be noticeably influenced by even very small changes in surface state (i.e., surface cleanliness).

The third task of the program related to the storage and delivery of liquid elemental mercury, used as a propellant in certain ion engines. The contact angle of mercury against six structural materials was measured over a specified range of temperatures likely to be encountered in use. The materials were stainless steel, nickel, tungsten, glass, quartz, and poly (tetrafluoroethylene). The temperatures were 25, 50, 75, 100, 125, and 150°C.

In addition to the writers, the following people contributed to this work: Mrs. Helein Bullard, Mr. Bernard Kidda, Mr. R. Bruce Klemm, Mr. George Lyerly and Mr. Henry Peper.

TASK I - EFFECT OF CONTAMINATION ON CONTACT ANGLE

A. Experimental

I. Materials

The solids, liquids and contaminants used in this work, their sources and/or specifications are tabulated in the Appendix.

II. Metal Surface Preparation

a. Metal Specimen Planchets

Cylindrical planchets, 1 in. diameter and 0.5 in. height were cut from 1 in. rod stock of aluminum alloy and titanium alloy. Stainless steel planchets were 1 in. diameter and .125 in. height since these were made from plate stock. The two faces of each planchet were made parallel and normal to the planchet axis by grinding with a Norton travelling bed surface grinder.

b. Metal Specimen Finishing

1. Fine grinding and pre-polishing -- After the planchet faces were surface ground, fine grinding was done by hand under water on

a Lunn-Labor wet grinding table beginning with number 220 grit silicon-carbide paper and finishing with number 600 grit silicon-carbide paper. Pre-polishing was done on a Fisher polishing wheel using Buehler No. 1 AB Polishing Alumina (aqueous slurry) on a Buehler AB silk Polishing Cloth followed by a finer polish using Buehler AB Gamma No. 3 Polishing Alumina (aqueous slurry) on a fresh AB Silk Cloth.

2. Fine polishing -- Planchet fine polishing was done on the Fisher polishing wheel using an aqueous slurry of Buehler Magomet on a Buehler Micropore cloth for the aluminum planchets and Buehler AB Gamma No. 3 Polishing Alumina on a Buehler Micropore cloth for the titanium and stainless planchets.

3. Satinizing -- Fine polished planchets were satinized for studies of the graphite contaminant by a sandblasting technique using 80-120 mesh silica blown by oil free nitrogen. The sandblasting apparatus consisted of an Erlenmyer suction filter flask (500 ml) containing the silica and fitted with a rubber stopper through which a loose fitting 30 cm. length of 10 mm. glass tubing was positioned so that its bottom touched the silica. The regulator gauge was set at 10 psig. The powdered silica was impinged against the planchet from a distance of six inches until uniform roughening had been obtained.

c. Metal Specimen Cleaning

Polished and satinized surfaces were given a final cleaning before use with aqueous detergent (Tide) solution. The specimens were immersed in the solution and the surfaces gently brushed using a soft camels hair brush. This was followed by thorough rinsing with hot tap water and finally with hot distilled water.

III. Application of Contaminant Films

Contaminants were mechanically spread over the surfaces of cleaned planchets and the material in excess of a thin film removed by wicking with filter paper and/or buffing with absorbent cotton. In the case of the graphite contaminant, the planchet surface was satinized to trap the graphite particles and the planchet was at room temperature. For all other contaminants the planchet surface was polished and the planchet was heated to about 90°C to facilitate removal of excess liquid (all of these contaminants are liquid at this temperature) by wicking.

IV. Contact Angle Measurements

Contact angles were determined as previously reported[1] by direct measurements on sessile drops of the above specified liquids resting on the above specified surfaces using the "NRL (Naval Research Laboratory) Contact Angle Goniometer".

The procedure was to place a drop of liquid on a surface and follow the change in contact angle as several small increments of the liquid were added and then withdrawn from the drop. During the addition process the angle builds up to a relatively constant value (within about ± 3°) which is termed the advancing contact angle. Similarly as liquid is withdrawn the angle declines to a constant value which is termed the receding contact angle.

Measurements of contact angles were made while the solid-liquid systems were in a thermostated optical cell. The temperature was controlled at 20 ± 0.5°C and the gas phase was air saturated with the vapor of the liquid in the cases of water and alcohol and dry nitrogen saturated with the vapor of the liquid in the cases of UDMH and IRFNA where reaction with moisture and CO_2 in air could interfere with the measurements.

A minimum of six individual measurements of both advancing and receding contact angles were made and averaged to obtain the reported values.

All measurements were made with the apparatus set up in a laminar flow clean hood as shown in Figure 1.

B. Results and Discussion

I. Water on Contaminated Metal Surfaces

Table I presents contact angle data for water on contaminated metal surfaces. The values obtained for the stearic acid "reference" contaminant agree with literature values showing the adequacy of the techniques and procedures used.

As indicated in Table I, high advancing contact angles and lower but still large receding contact angles were observed for water on all contaminants except graphite. Moderate advancing angles of about 45° and zero receding angles were observed for graphite. The data indicate that the water contact angle is determined by the contaminant film with the metal substrate having little or no effect.

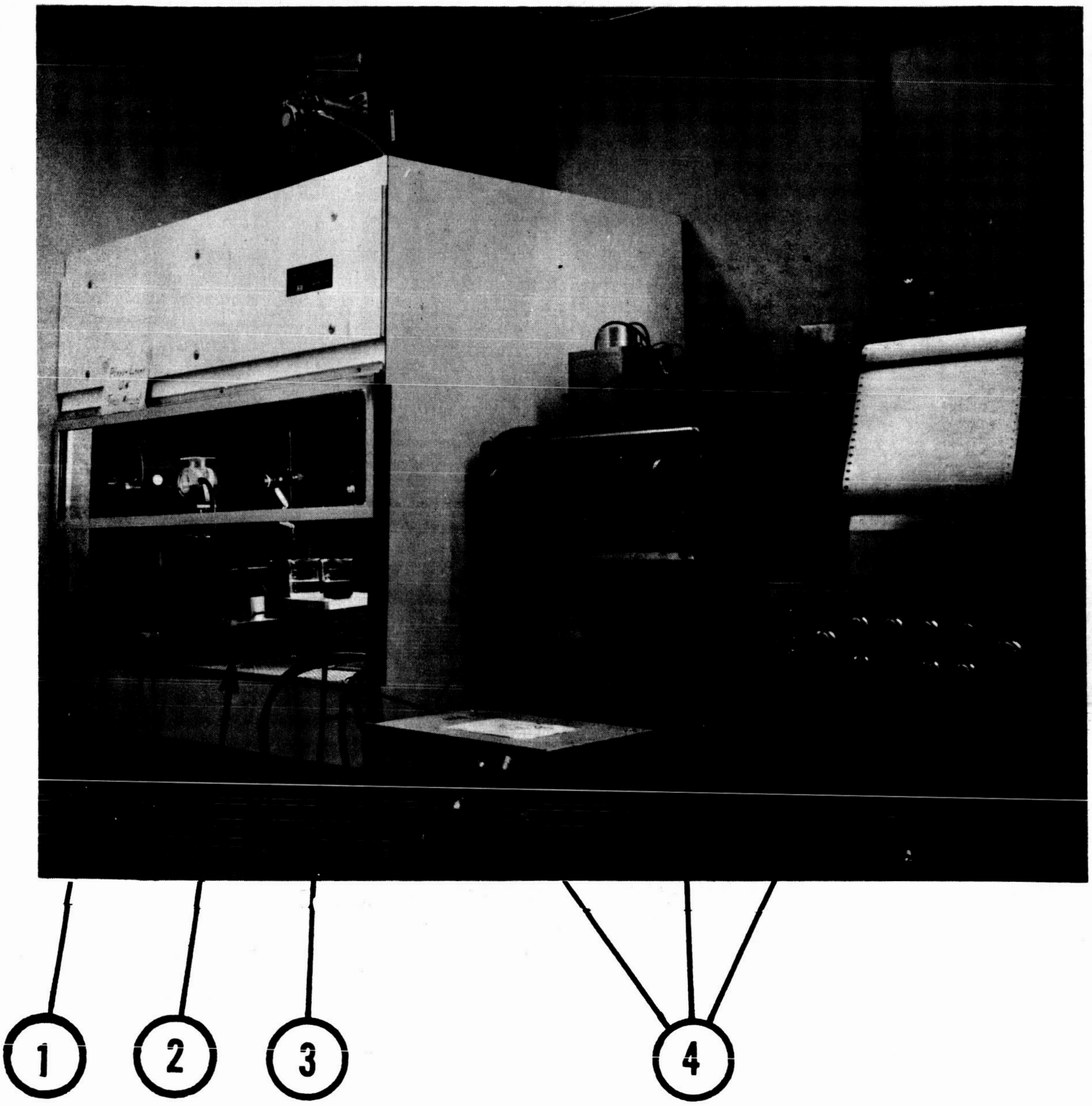
II. Ethanol on Contaminated Metal Surfaces

Table II presents contact angle data for ethanol on contaminated metal surfaces. With few exceptions advancing angles are zero. All receding angles are zero. The few finite advancing angles observed (stearic acid contaminant on all metals and the tristearin-triolein mxiture on stainless steel) are relatively small.

III. UDMH on Contaminated Metal Surfaces

Table III presents contact angle data for UDMH on the various contaminant-metal combinations. Only in the two cases of stearic acid contaminant

Figure 1. Equipment Used in Tasks I and II Including Laminar Flow Clean Hood



1. Contact angle goniometer
2. Radioactive electrode cell
3. Hot cleaning solutions
4. Equipment for measuring, calibrating, and recording surface potentials.

TABLE I

CONTACT ANGLES OF WATER ON CONTAMINATED METAL SURFACES

Contaminant	Type 301 Stainless Steel		6061T6 Aluminum Alloy		Grade 6 Titanium Alloy	
	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.
Stearic Acid	108	96	112	64	103	65
Oleic Acid	108	99	104	78	92	66
Tri-olein, Tri-stearin	94	85	96	73	90	66
Paraffin Oil	106	92	105	66	101	67
Naphthenic Oil	104	92	102	65	95	55
Asphalt	104	83	103	69	99	66
Graphite	44	0	45	0	46	0

TABLE II

CONTACT ANGLES OF ETHANOL ON CONTAMINATED METAL SURFACES

Contaminant	Type 301 Stainless Steel		6061T6 Aluminum Alloy		Grade 6 Titanium Alloy	
	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.
Stearic Acid	20	0	16	0	14	0
Oleic Acid	0	0	0	0	0	0
Tri-olein, Tri-stearin	10	0	0	0	0	0
Paraffin Oil	0	0	0	0	0	0
Naphthenic Oil	0	0	0	0	0	0
Asphalt	0	0	0	0	0	0
Graphite	0	0	0	0	0	0

TABLE III

CONTACT ANGLES OF UNSYMMETRICAL DIMETHYLHYDRAZINE ON CONTAMINATED METAL SURFACES

Contaminant	Type 301 Stainless Steel		6061T6 Aluminum Alloy		Grade 6 Titanium Alloy	
	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.
Stearic Acid	25	0	14	0	0	0
Oleic Acid	0	0	0	0	0	0
Tri-olein, Tri-stearin	0	0	0	0	0	0
Paraffin Oil	0	0	0	0	0	0
Naphthenic Oil	0	0	0	0	0	0
Asphalt	0	0	0	0	0	0
Graphite	0	0	0	0	0	0

on stainless steel and aluminum alloy were finite angles observed and these were advancing angles. The receding angles were all zero.

IV. IRFNA on Contaminated Metal Surfaces

As indicated in Table IV which presents contact angle data for IRFNA on the various contaminant metal combinations, all advancing and receding angles were zero or <5°. The value <5° means that the drop had a finite boundary when viewed from above but the angle was too small to be seen in the goniometer. Also in Table IV an initial value of contact angle is given for IRFNA on the various contaminant-metal combinations. Presumably IRFNA forms a finite contact angle with all of the contaminants on stainless steel and aluminum initially and almost immediately dissolves or chemically attacks the contaminant film and spreads on the underlying substrate.

C. Conclusions

There are two important conclusions to this work.

(1) Of the four liquids studied, only water formed large contact angles (both advancing and receding) with virtually all of the metal-contaminant combinations. The remaining 3 liquids showed zero receding angles on all metal-contaminant systems and with a few exceptions zero advancing angles as well.

(2) The solvent and/or oxidizing power of IRFNA enabled it to remove the organic film contaminant and spread on the underlying metal.

TABLE IV

CONTACT ANGLES OF INHIBITED RED FUMING NITRIC ACID ON CONTAMINATED METAL SURFACES

Contaminant	Type 301 Stainless Steel			6061T6 Aluminum Alloy			Grade 6 Titanium Alloy		
	Init.[1]	Adv.	Rec.	Init.[1]	Adv.	Rec.	Init.[1]	Adv.	Rec.
Stearic Acid	20	0	0	10	0	0	0	0	0
Oleic Acid	15	0	0	10	0	0	0	0	0
Tri-olein, Tri-stearin	20	0	0	10	0	0	0	0	0
Paraffin Oil	25	< 5	0	15	0	0	0	0	0
Naphthenic Oil	25	< 5	0	15	0	0	0	0	0
Asphalt	25	< 5	0	10	0	0	0	0	0
Graphite	0	0	0	0	0	0	0	0	0

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[1] The angle observed immediately after placing a drop of IRFNA on the surface; where this was finite it decreased rapidly to the advancing angle.

TASK II - EVALUATION OF CLEANING PROCEDURES

A. Experimental

I. Materials

The solid metals, liquids and contaminants were the same as described above under Task I. The metal surfaces were prepared for use in the same way and the contaminants were applied to the solid metal surfaces in the same manner.

II. Surface Cleaning Procedures

Approximately 85 companies were contacted by letter requesting information on procedures and materials for cleaning spacecraft tankage and ducts. Approximately half of those contacted replied and of these approximately half were unable to provide information. From the approximately 20 informative replies thus remaining the cleaning procedures to be evaluated were chosen.

It was decided that the cleaning procedures to be evaluated should meet the following requirements.

1. They should be actual cleaning procedures used in the industry.
2. They should not mechanically or chemically damage the finish of the metal surface.

After screening the procedures on the basis of these requirements a group of procedures was chosen for each metal to incorporate the widest possible variation in procedures. Finally, requirement 1 was relaxed to the extent that one or two hybrid procedures (the first part of one Company's procedures with the last part of another's) were included to provide the desired variation.

Tables V, VI and VII present the five cleaning procedures selected for stainless steel and the three each for aluminum alloy and titanium alloy respectively.

In general, the information received indicated that the cleaning procedures used for these metals following preliminary mechanical abrasion or acid descaling steps to remove gross surface coatings, comprised 2 or more of the following steps:

1. Degreasing with solvent or detergent
2. Treating with alkaline cleaning agent
3. Treating with acid cleaning agent

The recommended solvent for degreasing was usually a chlorinated solvent for steel and aluminum. The use of chlorinated solvents was prohibited with titanium and a hydrocarbon solvent was recommended. A great many proprietary alkaline cleaning agents were specified. The acid cleaning agent was moderate strength nitric acid with or without a chromate inhibitor. When both alkaline and acid cleaning steps were used, usually but not always the alkaline cleaner was used first. Alkaline and/or acid cleaning steps were always followed by water rinsing. The final step was drying which was sometimes aided by prior rinsing with a volatile solvent for water such as isopropanol.

III. Contact Angle and Surface Potential Measurements.

Contact angle data were obtained using the same procedure as outlined above for Task I.

Surface potential or contact potential was measured using a device built to duplicate the one described by K. W. Bewig (2). The experimental

TABLE V

CLEANING PROCEDURES FOR TYPE 301 STAINLESS STEEL

Procedure 1:
Step 1: Solvent degrease with trichloroethylene
Step 2: Alkaline clean with Cee Bee MX39, 140-180°F, 4-6 oz gal^{-1}, 20 min.
Step 3: Dry

Procedure 2:
Step 1: Solvent degrease with trichloroethylene
Step 2: Alkaline clean with Kelite 235, 180-200°F, 16-48 oz gal^{-1}, 60 min max.
Step 3: Passivate with 20-40% Aqueous nitric acid (40° Be) vol and 2-4% wt sodium dichromate.
Step 4: Dry

Procedure 3:
Step 1: Solvent degrease with trichloroethylene
Step 2: Passivate with nitric acid (commercial) 50-55% vol, at ambient, 30-45 min.
Step 3: Alkaline clean with Oakite NSS, 8% vol, 120-140°F, for 10-15 min.
Step 4: Rinse with isopropanol (99.9%, commercial)
Step 5: Dry

Procedure 4:
Step 1: Solvent degrease with trichloroethylene
Step 2: Alkaline clean with Kelite 235, 180-200°F, 16-48 oz gal^{-1}, 60 min max.
Step 3: Dry

Procedure 5:
Step 1: Solvent degrease with trichloroethylene
Step 2: Passivate with nitric acid (30% by volume) containing 4 oz gal^{-1} sodium dichromate at 120-140°F for 20 min.
Step 3: Dry

---

[1] Specific gravity of undiluted nitric acid is 40° Baume equivalent to 61.38%.
Unless otherwise specified, solution percent concentrations refer to precent of non-diluted concentrated nitric acid.

TABLE VI

CLEANING PROCEDURES FOR 6061T6 ALUMINUM ALLOY

Procedure 1:
- Step 1: Solvent degrease with trichlorethylene at ambient for 5 min.
- Step 2: Passivate with 50-55% nitric acid[1] at ambient for 30-45 min.
- Step 3: Neutralize with Oakite NSS, 8% by vol, at 130°F for 15 min.
- Step 4: Solvent rinse with isopropanol
- Step 5: Dry

Procedure 2:
- Step 1: Solvent degrease with trichloroethylene at ambient for 5 min.
- Step 2: Mild alkaline clean with Oakite NSS, 8% by vol, at 130°F for 15 min.
- Step 3: Passivate with 50-55% nitric acid at ambient for 30-45 min.
- Step 4: Dry

Procedure 3:
- Step 1: Solvent degrease with trichloroethylene at ambient for 5 min.
- Step 2: Alkaline clean with Cee Bee MX39, 3.7 oz gal^{-1} at 180°F for 20 min.
- Step 3: Dry

---

[1] Unless otherwise specified, solution concentrations refer to volume percent of non-diluted concentrated nitric acid.

TABLE VII

CLEANING PROCEDURES FOR GRADE 6 TITANIUM ALLOY

Procedure 1:

Step 1: Detergent degrease with Oakite NSS, 8% (vol), at 130°F for 5 min (minimum)
Step 2: Passivate with 55% (vol) nitric acid (commercial) at ambient for 45 min.
Step 3: Alkaline clean with Oakite NSS, 8% (vol), at 130°F for 15 min.
Step 4: Rinse with 99.9% isopropanol
Step 5: Dry

Procedure 2:

Step 1: Alkaline clean with Oakite 77, 8 oz. gal^{-1} at 180°F for 20 min.
Step 2: Passivate with 40% nitric acid (vol)(43° Be) at ambient for 2 min.
Step 3: Dry

Procedure 3:

Step 1: Solvent degrease with toluene at ambient for 5 min.
Step 2: Alkaline soak clean with Alkon at 180°F for 20 min.
Step 3: Passivate with 30% nitric acid (by vol) containing 4 oz gal^{-1} sodium dichromate.
Step 4: Dry

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[1] Specific gravity of undiluted nitric acid is 43° Baume equivalent to 70.33%. Unless otherwise specified, solution percent concentrations refer to percent of non-diluted concentrated nitric acid.

set-up appears in Figure 1. This instrument uses the radioactive electrode or ionization method of determining surface potential.

Surface potential is highly sensitive to minute changes in surface conditions. Thus when this measurement is carried out on surfaces in the presence of the laboratory atmosphere and after rather harsh polishing and cleaning procedures, a relatively poor degree of reproducibility can be expected. Thus potential data are reported in a manner indicating the variation in values obtained at various times and with different specimens used during the course of the work.

B. Results and Discussion

I. Stainless Steel

Table VIII presents contact angle and surface potential data which reflect the effect of five cleaning procedures on contaminated stainless steel. For convenience, contact angles of water and alcohol on contaminated surfaces from Table I and II are repeated in Table VIII.

All of the cleaning procedures are very effective in increasing the water wettability of contaminated surfaces. The graphite contaminant, as might be expected, was less affected by the cleaning procedures than the other contaminants. While it appears that certain cleaning procedures are slightly more effective than others with respect to specific contaminants, none of the cleaning procedures appears to be significantly more effective on all types of contaminant. In the few cases where the advancing contact angle of alcohol on contaminated surfaces was finite, all of the cleaning procedures were able to render these contaminated surfaces alcohol wettable (zero contact angle).

TABLE VIII

EFFECT OF CLEANING PROCEDURES ON CONTACT ANGLES AND SURFACE POTENTIALS OF CONTAMINATED TYPE 301 STAINLESS STEEL

Contaminant Type	Cleaning Procedure[1]	Water Contact Angle				Alcohol Contact Angle				Surface Potential (millivolts)[2]		
		Contaminated		Cleaned		Contaminated		Cleaned		Prepared[3]	Contaminated	Cleaned
		Adv	Rec	Adv	Rec	Adv	Rec	Adv	Rec			
Stearic Acid	1	108	96	3	< 2	20	0	0	0	-133±24	+169± 24	- 55±378
Oleic Acid		108	99	3	< 3	0	0	0	0	"	+103± 17	- 19±228
Tri-stearin Tri-olein		94	85	4	< 3	10	0	0	0	"	+203± 34	+ 25±162
Naphthenic Oil		104	92	7	0	0	0	0	0	"	+210± 33	+ 33±360
Paraffin Oil		106	92	13	5	0	0	0	0	"	+205± 13	+ 57±421
Asphalt		104	83	8	3	0	0	0	0	"	+174± 21	+258±135
Graphite		44	0	26	0	0	0	0	0	-254±35	-106±163	+167± 80
Stearic Acid	2	108	96	21	< 3	20	0	0	0	-133±24	+169± 24	-158±397
Oleic Acid		108	99	21	< 3	0	0	0	0	"	+103± 17	-367±293
Tri-stearin Tri-olein		94	85	17	6	10	0	0	0	"	+203± 34	-254±134
Naphthenic Oil		104	92	10	< 3	0	0	0	0	"	+210± 33	-231±289
Paraffin Oil		106	92	8	3	0	0	0	0	"	+205± 13	-396±401
Asphalt		104	83	10	3	0	0	0	0	"	+174± 21	-505±609
Graphite		44	0	30	0	0	0	0	0	-254±35	-106±163	-536±172
Stearic Acid	3	108	96	22	< 3	20	0	0	0	-133±24	+169± 24	- 61±236
Oleic Acid		108	99	18	< 3	0	0	0	0	"	+103± 17	+ 70±298
Tri-stearin Tri-olein		94	85	21	< 3	10	0	0	0	"	+203± 34	+ 19±228
Naphthenic Oil		104	92	16	< 3	0	0	0	0	"	+210± 33	+ 6±333
Paraffin Oil		106	92	10	3	0	0	0	0	"	+205± 13	+ 81±379
Asphalt		104	83	11	3	0	0	0	0	"	+174± 21	+ 66±237
Graphite		44	0	29	0	0	0	0	0	-254±35	-106±163	-407±221

TABLE VIII (Contd)

Contaminant Type	Cleaning Procedure[1]	Water Contact Angle				Alcohol Contact Angle				Surface Potential (millivolts)[2]		
		Contaminated		Cleaned		Contaminated		Cleaned		Prepared[3]	Contaminated	Cleaned
		Adv	Rec	Adv	Rec	Adv	Rec	Adv	Rec			
Stearic Acid	4	108	96	22	< 3	20	0	0	0	-133±24	+169± 24	+ 23± 43
Oleic Acid		108	99	19	< 3	0	0	0	0	"	+103± 17	+266±202
Tri-stearin Tri-olein		94	85	24	< 3	10	0	0	0	"	+203± 34	+ 84±270
Naphthenic Oil		104	92	42	21	0	0	0	0	"	+210± 33	+131± 35
Paraffin Oil		106	92	22	5	0	0	0	0	"	+205± 13	+119±189
Asphalt		104	83	15	8	0	0	0	0	"	+174± 21	+180±178
Graphite		44	0	10	0	0	0	0	0	-254±35	-106±163	+192± 86
Stearic Acid	5	108	96	14	0	20	0	0	0	-133±24	+169± 24	-169±166
Oleic Acid		108	99	15	0	0	0	0	0	"	+103± 17	-224± 95
Tri-stearin Tri-olein		94	85	28	< 3	10	0	0	0	"	+203± 34	- 77±191
Naphthenic Oil		104	92	7	< 3	0	0	0	0	"	+210± 33	-273±260
Paraffin Oil		106	92	19	5	0	0	0	0	"	+205± 13	-434±252
Asphalt		104	83	24	3	0	0	0	0	"	+174± 21	-204±356
Graphite		44	0	12	0	0	0	0	0	-254±35	-106±163	-749±190

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[1] Refer to TABLE V

[2] Results given are averages and 95% confidence interval

[3] Polished by methods in EXPERIMENTAL Section

Analysis of the surface potential data in Table VIII provides the following observations. Surface potential values for prepared (polished and detergent cleaned) and contaminated surfaces are reasonably reproducible whereas those for cleaned surfaces (contaminated surfaces subjected to a cleaning procedure) are poorly reproducible. The values for graphite are a special case because of the use of satinized planchets. The prepared and contaminated surface potential values are easily distinguishable from one another. On the other hand the values for cleaned surfaces were so poorly reproducible that repeated determinations ranged all the way from prepared to contaminated surfaces and frequently further. This data, therefore, does not provide a satisfactory means of evaluating cleaning procedures. The satisfactory reproducibility of measurements on prepared and contaminated samples indicates that the method is capable of detecting the presence of contaminants of the type investigated. Thus the results on cleaned surfaces are interpreted to mean that the cleaning procedures leave random residues on the solid surfaces to which the surface potential is very sensitive and the contact angle practically insensitive.

II. Aluminum Alloy

Table IX presents contact angle and surface potential data which reflect the effect of three cleaning procedures on contaminated aluminum alloy. The format of Table IX is the same as that for Table VIII which was described above.

The contact angle data indicate that these cleaning procedures for aluminum alloy are about as effective as were the procedures for stainless steel. Procedure 3 appears to be more effective with respect to water contact angle lowering than procedures 1 or 2 although the difference is relatively small.

TABLE IX

EFFECT OF CLEANING PROCEDURES ON CONTACT ANGLES AND SURFACE POTENTIALS OF CONTAMINATED 6061T6 ALUMINUM ALLOY

Contaminant Type	Cleaning Procedure[1]	Water Contact Angle				Alcohol Contact Angle				Surface Potentials (millivolts)[2]		
		Contaminated		Cleaned		Contaminated		Cleaned		Prepared[3]	Contaminated	Cleaned
		Adv	Rec	Adv	Rec	Adv	Rec	Adv	Rec			
Stearic Acid	1	112	64	14	0	16	0	0	0	+350±28	+1,307±29	+288±117
Oleic Acid		104	78	8	0	0	0	0	0	"	+1,480±82	+659±520
Tri-stearin Tri-olein		96	73	14	0	0	0	0	0	"	+1,374±63	+512±260
Paraffin Oil		105	66	18	0	0	0	0	0	"	+1,362±28	+422± 52
Naphthenic Oil		102	65	8	0	0	0	0	0	"	+1,350±29	+446± 55
Asphalt		103	69	23	0	0	0	0	0	"	+1,389±58	+502±139
Graphite		44	0	28	0	0	0	0	0	+269±34	- 182±63	+572±155
Stearic Acid	2	112	64	21	0	16	0	0	0	+350±28	+1,307±29	+579±140
Oleic Acid		104	78	17	0	0	0	0	0	"	+1,480±82	+440± 70
Tri-stearin Tri-olein		96	73	24	0	0	0	0	0	"	+1,374±63	+634±265
Paraffin Oil		105	66	17	0	0	0	0	0	"	+1,362±28	+462±286
Naphthenic Oil		102	65	15	0	0	0	0	0	"	+1,350±29	+638±228
Asphalt		103	69	11	0	0	0	0	0	"	+1,389±58	+456±306
Graphite		44	0	29	0	0	0	0	0	+269±34	- 182±63	+346±154
Stearic Acid	3	112	64	8	0	16	0	0	0	+350±28	+1,307±29	+700±526
Oleic Acid		104	78	6	0	0	0	0	0	"	+1,480±82	+596±534
Tri-stearin Tri-olein		96	73	4	0	0	0	0	0	"	+1,374±63	+814±256
Paraffin Oil		105	66	3	0	0	0	0	0	"	+1,362±28	+864±649
Naphthenic Oil		102	65	4	0	0	0	0	0	"	+1,350±29	+719±236
Asphalt		103	69	5	0	0	0	0	0	"	+1,389±68	+870± 93
Graphite		44	0	0	0	0	0	0	0	+269±34	- 182±63	+400±198

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[1] Refer to TABLE VI

[2] Results given are averages and 95% confidence interval

[3] Polished by methods in EXPERIMENTAL Section

In the few cases where finite alcohol contact angles were observed on contaminated aluminum alloy all three cleaning procedures brought about a reduction in the contact angle to zero.

Surface potentials followed a pattern similar to that observed with stainless steel. That is, good reproducibility of measurements for prepared and contaminated surfaces and poor reproducibility for the cleaned surfaces. The values for the surface potential for prepared and contaminated surfaces are of course different from those obtained with stainless steel. The poor reproducibility of the values for cleaned surfaces again indicates that reagents used in these cleaning procedures leave random residues on the surfaces which have a large effect on surface potential and a negligible effect on contact angle.

III. Titanium Alloy

Table X presents contact angle and surface potential data for the cleaning procedures evaluation with contaminated titanium alloy. The format is again the same as that used for Tables VIII and IX.

Essentially the same pattern of results both with respect to contact angle and surface potential as was observed with stainless steel is shown in Table X. Procedures 1 and 3 appear to be a little more effective than procedure 2 as indicated by water contact angles but this difference is indeed small.

Surface potential values tend to be more like those for steel which is in contrast to the values for aluminum which were significantly different than those for steel. Again, poor reproducibility of the values for cleaned surfaces is observed suggesting the existence of residues from the cleaning agents.

TABLE X

EFFECT OF CLEANING PROCEDURES ON CONTACT ANGLES AND SURFACE POTENTIALS OF CONTAMINATED GRADE 6 TITANIUM ALLOY

Contaminant Type	Cleaning Procedure[1]	Water Contact Angle				Alcohol Contact Angle				Surface Potentials (millivolts)[2]		
		Contaminated		Cleaned		Contaminated		Cleaned		Prepared[3]	Contaminated	Cleaned
		Adv.	Rec	Adv	Rec	Adv	Rec	Adv	Rec			
Stearic Acid	1	103	65	9	< 3	14	0	0	0	-160±43	+457± 47	+198±218
Oleic Acid		92	66	10	0	0	0	0	0	"	+564± 29	+219±101
Tri-stearin Tri-olein		90	66	13	0	0	0	0	0	"	+770± 60	+277±246
Paraffin Oil		101	67	11	0	0	0	0	0	"	+600± 81	+269± 74
Naphthenic Oil		95	55	10	0	0	0	0	0	"	+730±110	+124±106
Asphalt		99	66	13	0	0	0	0	0	"	+672± 17	+207± 73
Graphite		46	0	34	0	0	0	0	0	-144±68	-147± 79	+206± 90
Stearic Acid	2	103	65	16	< 3	14	0	0	0	-160±43	+457± 47	+192±167
Oleic Acid		92	66	16	0	0	0	0	0	"	+564± 29	+139±140
Tri-stearin Tri-olein		90	66	22	0	0	0	0	0	"	+770± 60	+ 61±102
Paraffin Oil		101	67	20	0	0	0	0	0	"	+600± 81	+ 34±264
Naphthenic Oil		95	55	32	3	0	0	0	0	"	+730±110	+112±308
Asphalt		99	66	22	0	0	0	0	0	"	+672± 17	+165±408
Graphite		46	0	24	0	0	0	0	0	-144±68	-147± 79	-145±111
Stearic Acid	3	103	65	7	< 3	14	0	0	0	-160±43	+457± 47	-111± 27
Oleic Acid		92	66	10	0	0	0	0	0	"	+564± 29	-120±304
Tri-stearin Tri-olein		90	66	9	0	0	0	0	0	"	+770± 60	-194±127
Paraffin Oil		101	67	9	0	0	0	0	0	"	+600± 81	-226±196
Naphthenic Oil		95	55	9	0	0	0	0	0	"	+730±110	-274±209
Asphalt		99	66	13	0	0	0	0	0	"	+672± 17	-114± 29
Graphite		46	0	14	0	0	0	0	0	-144±68	-147± 79	-324±104

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[1] Refer to TABLE VIII

[2] Results given are averages and 95% confidence interval

[3] Polished by methods in EXPERIMENTAL Section

C. Conclusions

All of the cleaning procedures investigated for each of the three metals were reasonably effective in rendering contaminated surfaces hydrophilic. None were completely effective and no one was clearly superior over another. In the few cases for each metal where the contaminated surfaces were alcohol-phobic, all cleaning procedures were able to render the surfaces alcohol-philic.

TASK III - EFFECT OF TEMPERATURE ON THE CONTACT ANGLE OF MERCURY

A. Experimental

I. Materials

a. Solids

1. Stainless steel, Type 347

2. Nickel, electrolytic grade

3. Tungsten, essentially pure with following limits on impurities.

Not more than 100 PPM total of Li, Na, K, and Rb

Not more than 15 PPM total of Cu

Not more than 10 PPM total of Ag

Not more than 100 PPM total of Ca*, Sr, Ba, Be, and Mg.

Not more than 75 PPM total of B and Al

Not more than 150 PPM total of C**, Si***, Sn, Pb*, Ti, Zr, Hf*, and Th*.

Not more than 50 PPM total of Sb* and Bi

Not more than 200 PPM total of Cr and Mo

Not more than 25 PPM total of Mn

Not more than 150 PPM total of Fe****, Co, Ni****, Ru, Rh, Pd, Os, Ir and Pt.

*Emission spectrograph "limit of detection" levels are acceptable. **30 PPM max., ***20 PPM max., ****50 PPM max.

4. Glass, "Pyrex" Brand Chemical Glass No. 7740

5. Quartz, fused

6. Teflon

b. Liquid

1. Mercury, triple distilled

III. Solid Surface Preparation.

Steel, nickel and glass specimens were cut, ground flat and polished using the same procedures as were used to prepare surfaces for Task I. Tungsten samples were supplied by NASA, and were specular films on metal supports. Quartz specimens were received from the supplier in a polished condition. Teflon surfaces were prepared by abrading specimens on #600 grit carborundum paper and polishing to a specular finish on a wheel covered with silk cloth wet with water.

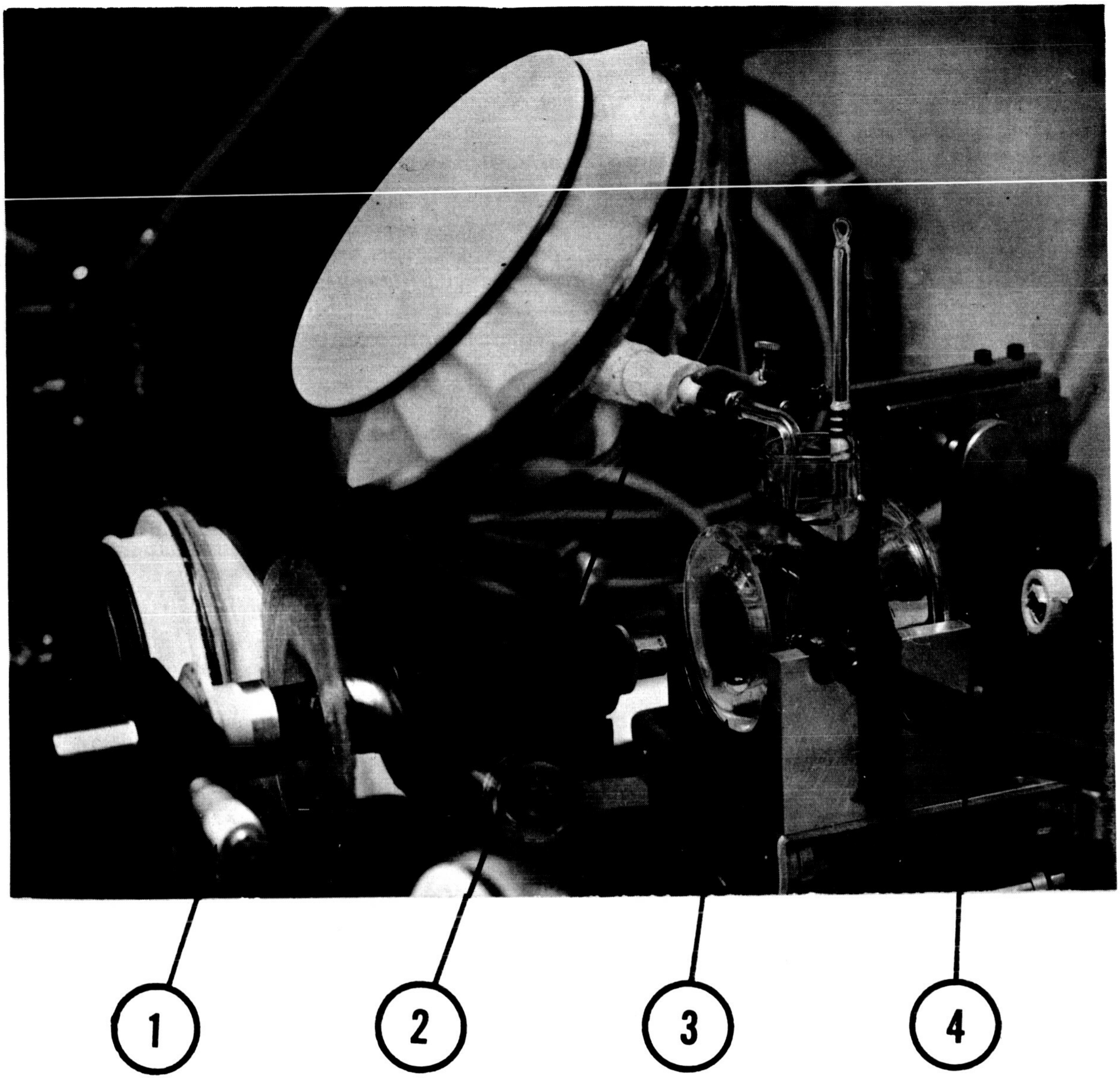
All specimens were given a final detergent cleaning before use as described above under Task I.

IV. Contact Angle Measurements

Contact angles were measured by direct measurements on sessile drops using a contact angle goniometer patterned after the "NRL" goniometer used and described under Task I. Measurements were made while the solid/mercury system was in a thermostated optical cell. The temperature was controlled by circulating silicone fluid through the cell from a constant temperature bath. The bath was regulated so as to produce the desired temperature of 25, 50, 75, 100, 125 or 150°C in the cell. A mercury thermometer was used to determine and monitor the temperature in the cell.

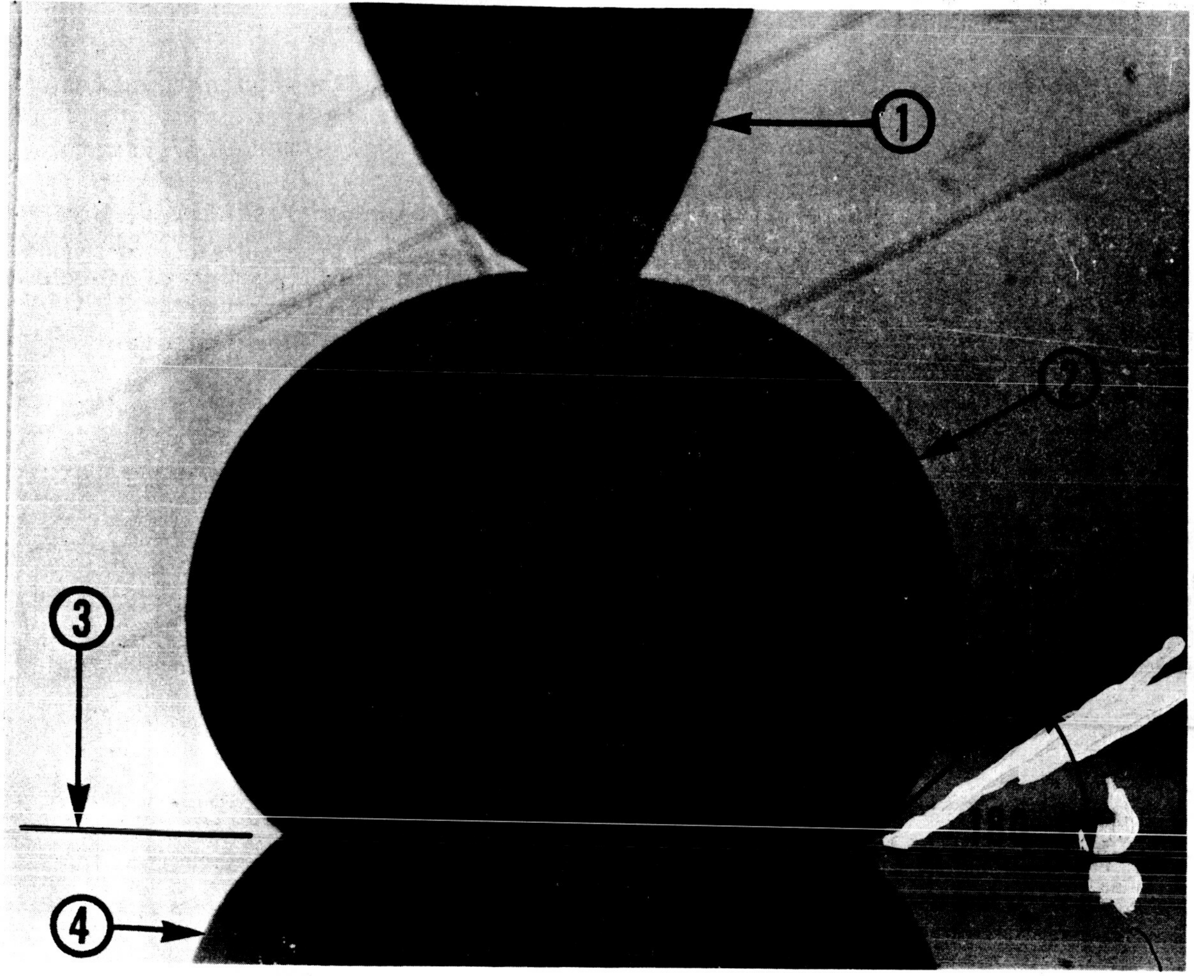
The contact angle thermostated cell was placed in a controlled atmosphere glove box enclosure in order to provide an atmosphere of dry nitrogen for the solid/mercury systems. A close-up view of the apparatus is shown in Figure 2. Figure 3 shows the appearance of a mercury drop as viewed through the goniometer. In preparation for measurements the enclosure was flushed with dry nitrogen until the atmosphere was at least 99.5% N_2. During measurements a recirculation system was put into operation which maintained

Figure 2. APPARATUS FOR OBSERVING CONTACT ANGLES OF MERCURY ON SOLID SURFACES.



1. Goniometer telescope used for observing contact angles.
2. Micropipette used for adding or withdrawing mercury.
3. Thermostated glass cell used to maintain constant temperature environment.
4. Micromanipulator used to position the micropipette.

Figure 3. MERCURY DROP PROFILE AS OBSERVED THROUGH THE CONTACT ANGLE GONIOMETER



1. Pipette to add or withdraw mercury.
2. Mercury drop.
3. Surface plane of solid specimen.
4. Reflection of mercury drop on surface plane of solid specimen.

this atmosphere. A schematic diagram of the gas flushing and circulation systems is shown in Figure 4. Analyses of the gas atmosphere within the enclosure were accomplished by gas chromatography using a 13X molecular sieve column at a constant temperature of 28°C.

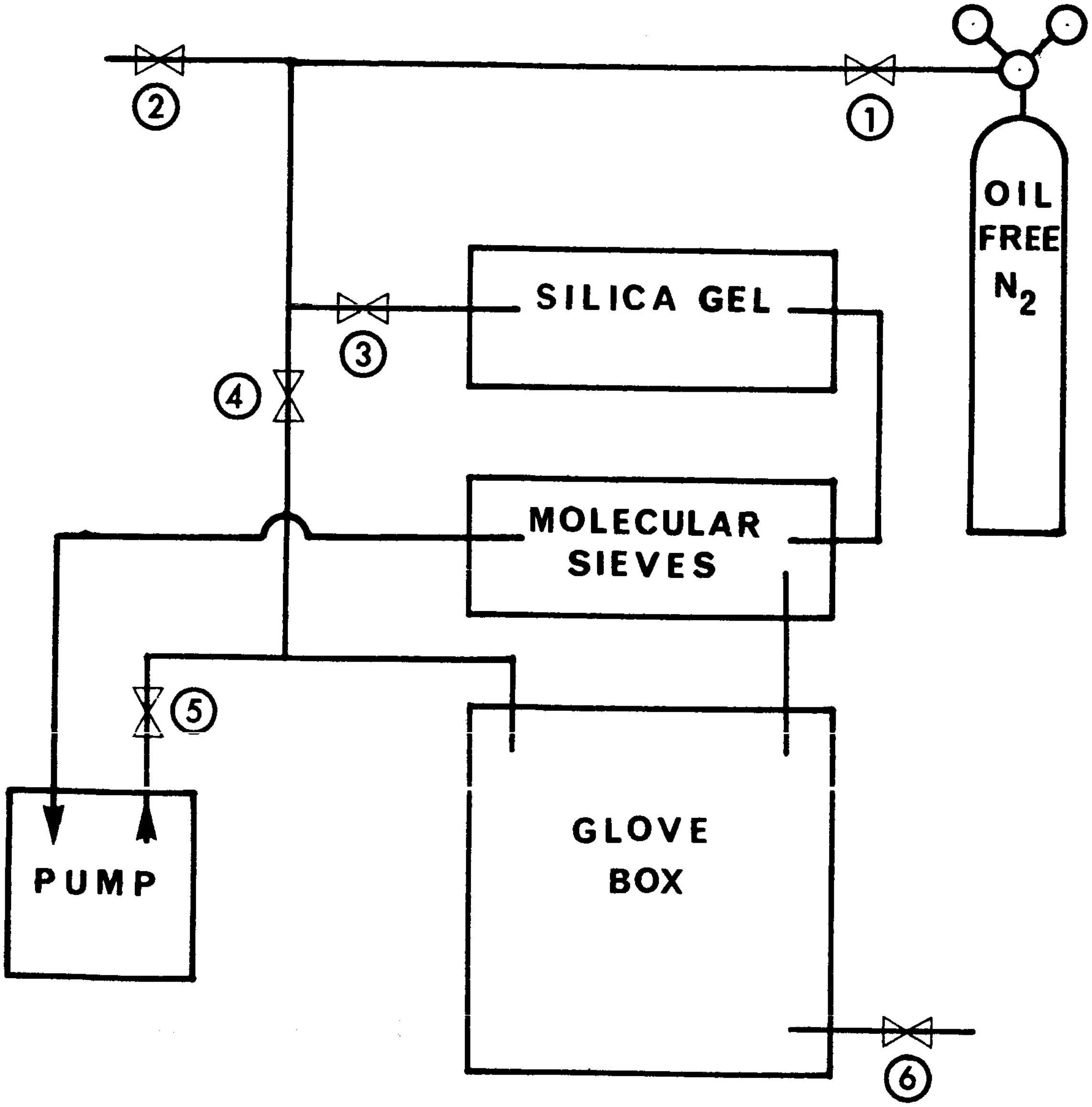
The procedure for obtaining advancing and receding contact angles as described under Task I was followed. With these solid/mercury systems, however, the advancing and receding angles as defined under Task I were not stable. The angle observed immediately after adding a small amount of mercury to the drop or the advancing angle, decreased steadily to a lower constant value. Likewise, the angle observed immediately after withdrawing a small increment from the drop, or the receding angle, increased steadily to a larger constant value. It was decided that all four angles should be reported, i.e., (1) the maximum angle observed immediately following an incremental addition of mercury to a sessile drop in the course of several such additions, or the maximum advancing angle, (2) the equilibrium advancing angle or the constant angle to which the maximum advancing angle falls, (3) the minimum receding angle which corresponds to the maximum advancing angle and (4) the equilibrium receding angle or the constant angle to which the receding angle rises.

It should be noted that the decay or change of the initially observed advancing and receding angles to the equilibrium values took place rather rapidly, usually within 10-30 seconds, and was probably accelerated by the slight inherent vibration in the system.

B. Results and Discussion

Table XI presents the contact angles of mercury on the six solid surfaces at the six temperatures. All of the angles are high and very little difference

Figure 4. A non-scale schematic sketch of the gas flushing and circulating system for the enclosure used for mercury contact angles.



The system operates:

Flushing		
Valve	1	Open
Valve	4	Open
Valve	6	Open

All others closed

Circulating		
Valve	1	Open
Valve	3	Open
Valve	5	Open
Valve	6	Open

All others closed

Valve 2 is an excess pressure vent

TABLE XI

CONTACT ANGLES OF MERCURY ON POLISHED SOLID SUBSTRATES AT VARIOUS TEMPERATURES

Solid Surface	Measurement Temperature						Range in degrees of angle, 25°-150°C
	25°C	50°C	75°C	100°C	125°C	150°C	
Tungsten							
Max adv	142	150	155	155	159	160	5-11
Equil adv	130	130	140	137	140	137	
Equil rec	132	132	137	135	141	137	
Min rec	121	110	120	119	123	124	
Stainless Steel							
Max adv	146	150	151	158	162	157	8-14
Equil adv	133	134	136	146	142	141	
Equil rec	132	134	138	143	144	141	
Min rec	124	121	120	130	132	130	
Nickel							
Max adv	148	150	156	161	160	165	6- 8
Equil adv	139	135	138	146	145	145	
Equil rec	138	134	137	146	146	145	
Min rec	123	116	124	129	133	130	
Quartz							
Max adv	147	144	150	152	155	159	2- 4
Equil adv	132	132	124	130	132	136	
Equil rec	134	132	122	131	132	136	
Min rec	115	122	110	122	118	114	
Glass							
Max adv	147	147	152	156	154	159	6- 7
Equil adv	133	132	132	136	139	140	
Equil rec	134	130	131	137	137	140	
Min rec	122	112	120	125	126	125	
TFE							
Max adv	157	162	166	169	175	178	12-15
Equil adv	134	135	137	142	146	147	
Equil rec	132	132	134	145	145	146	
Min rec	104	98	109	119	119	116	

is observed between the "high energy" surfaces of tungsten, steel, nickel, quartz and glass and the "low energy" surface of Teflon. The variation in contact angle with temperature is very small for all solid/mercury systems. Only in the case of Teflon is the variation significantly larger than the accepted experimental error in contact angle measurements. The slope of the contact angle-temperature relation although small is positive with all solid/mercury systems. It is quite reasonable that the temperature coefficient of the contact angle should be small since the temperature coefficients of the interfacial tensions acting at the three phase boundary (which determine the contact angle) should be almost equal.

It can be seen from Table XI that the equilibrium advancing and equilibrium receding angles are the same and also just about at the arithmetic mean of the maximum advancing and minimum receding angles. The significance of this, if any, is not apparent.

For each solid/mercury-temperature combination the four angles were reported because it was believed that any one might be important depending upon the application. In terms of relating this data to other contact angle data in the literature it appears probable that the maximum advancing angle should be used. This recommendation is based on the fact that the value for Teflon/mercury at 25°C in Table XI (157°) checks quite well with the literature value (150°) (3).

C. Conclusions

There are two important conclusions to the Task III work.

1. Mercury forms large contact angles, of the order of 150°, with all of the solid surfaces studied.

2. The contact angle of mercury on the various solid surfaces studied increases very slightly, i.e., about 10 or 15° over the temperature range of 25 to 150°C.

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APPENDIX

TABLE XII - MATERIALS

a. Solids

1. Stainless Steel, Type 301
2. Aluminum alloy, Type 6061T6
3. Titanium alloy, 5% Aluminum, 2.5% Tin, ASTM B 265-58T Grade 6

b. Liquids

1. Water, Free of organic matter, inorganic contamination less than 0.5 ppm, resistance no less than 0.6 megohms per cc at 20°C.
2. Ethanol, Chemically pure, undenatured, anhydrous (200 proof)
3. Unsymmetrical - Dimethyl - Hydrazine (UDMH) Mil Spec. D-25604B
4. Inhibited Red Fuming Nitric Acid (IRFNA) Mil Spec P-7254E(IIIB)

c. Contaminants

1. Stearic Acid - Octadecanoic Acid, Armour Research Division, Armour and Co., Lot 421-281.

   This material was chosen as a reference contaminant. It would produce a film of a pure chemical the wetting of which by water has been reported in the literature.
2. Oleic Acid - "Purified" Fisher Scientific Co., Lot No. 733324.
3. Mixture of Tri-stearin (25% wt.)(#1380 Distillation Products Industries) and Tri-Olein (Wilmar Glyceryl trioleate,

Wilson-Martin Division, Wilson and Co., Inc.

These materials were chosen since they are constituents of human skin oils that might be transferred to rocket tankage in handling.

4. Paraffin Oil - USP, Fisher Scientific Co., Lot No. 745017

5. Naphthenic Oil - Circo Med Oil, Sun Oil Company.

These materials were chosen as representative of cutting and grinding oils that might be left on rankage following these operations.

6. Asphalt - #3950 Road Aggregate Sample from Nationa Bureau of Standards.

7. Graphite - Technical grade, Fisher Scientific Company, Lot No. 784024.

These materials were chosen as typical of the residue that would be left on tankage following prolonged exposure to atmospheric contaminants.