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Surface Cleaning by Glow Discharge in a High-Volume Gas Flow

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Surfaces of solids and the surfaces of domains within the solids are generally coated with contaminents which determine many of the mechanical properties of those surfaces (such as the ability to cold weld). This report describes a technique of cleaning the solid surface by continually purging a glow-discharge chamber with ultraclean, dry, and chemically inert gas during the flow-discharge phase. A large vacuum chamber is used which is 81 centimeters in diameter and 3 meters long. The purging gas is allowed to flow through the chamber, past the sample holder, at a rate of about 3

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chamber volumes per minute. Such a large chamber is used instead of standard commercial glow-discharge devices to allow for many mean free paths for the contaminents to expand into and thus increase the time required to contact the chamber walls. This allows the sweeping action of the gas flow to move the contaminants downstream and thus reduce the probability of recontaminating either the chamber walls or the test surfaces. The cleaning effectiveness is compared by measuring the contact angles that high-surface-energy liquid drops make with the cleaned surface. The liquids used are triply distilled water for detecting hydrophobic contamination and methylene iodide for detecting water contamination. The surfaces used to demonstrate the cleaning technique were stainless steel and aluminum oxide. Some of the contact angles were too flat to observe but were estimated to be less than 1°. The small contact angles are intrepreted to mean that there is less than 1 monomolecular layer of contaminant on the cleaned surface.

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CONTENTS

SURFACE CLEANING BY GLOW DISCHARGE IN A HIGH-VOLUME GAS FLOW

INTRODUCTION

The problem of obtaining a surface which is uncontaminated by foreign substances (materials different from that of the pure surface) which may be adsorbed on the surface, such as water and the hydrocarbons common to the atmosphere, has been approached in many ways. Chemical cleaning, at the least, leaves a film of the final-rinse material. Sputtering a layer off the surface, leaving a clean layer, changes the structure of the surface. Sputtering on a new layer covering over the old surface with all its contamination (sweeping it under the rug) also changes the structure with no assurance that the new layer will not peel off. A "bakeout" may "bake on" the unknown substances initially contaminating the surface, depending on the contaminating substances and the nature of the material of the surface itself.

The problem has been discussed by many writing about vacuum systems, cleaning techniques, and their uses. Some of these authors are referenced [1-12] and have been valuable sources of information. Bombardment of the surface is common to the cleaning of surfaces, by both kinds of sputtering, off or on, and by "glow discharge," however the sputtering-off technique uses high-energy bombardment, whereas a glow-discharge method uses comparitively low energy particles (between 1 and 10 electron volts).

Previous use of ion bombardment has resulted in a limited cleaning action, because the atmosphere seems to become saturated with the contaminants from both the object to be cleaned and from the vacuum system it is being cleaned in. The result has been that the sample to be cleaned has been known to reach a condition of maximum cleanliness, after which further ion bombardment releases subsurface contaminants and the object becomes more contaminated.

The purpose of this report is to describe the hardware and the operation of a modified low-energy glow-discharge cleaning system and to report the results of the tests and subsequent conclusions about the effectiveness of the cleaning process. The purpose of this glow-discharge cleaning system is to demonstrate a system which will not recontaminate the cleaned sample and will eliminate the uncertainty of estimating the proper cleaning time for removing the test sample at its minimum contamination level.

PROCEDURES AND RESULTS

If a glow-discharge cleaning system will saturate with contaminants and recontaminate the object to be cleaned, then the best approach is to remove the contamination from the system as it is released from the surface of both the chamber and the object. Therefore the first modification to the cleaning system was allowing the glow-discharge gas to flow

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through the chamber past the object and out through a cold trap. The rate of flow was the equivalent of at least 3 chamber volumes of gas per minute.

The second modification was to choose a chamber large enough so that there would be enough mean free paths between the walls of the chamber and the position of the sample to be cleaned to reduce the probabilities of recontamination of the chamber or of the sample by the newly released contaminants. (The details of the vacuum system are described in Appendix A, and the cleaning system is described in Appendix B.)

The third modification was in the procedure of backfilling the chamber with clean dry extra-pure nitrogen gas, which was also passed through a cooling coil immersed in a slurry of dry ice and acetone and then was reheated in a second coil before passing into the cleaning chamber. The idea was to trap what moisture and other impurities may have been left in the gas.

The fourth modification involved the procedure for measuring the contact angles (illustrated and explained in Fig. 1). A goniometer was combined with a 90-mm-focal-length lens on a small optical bench (Appendix C, Fig. C1b) so that the drops inside a

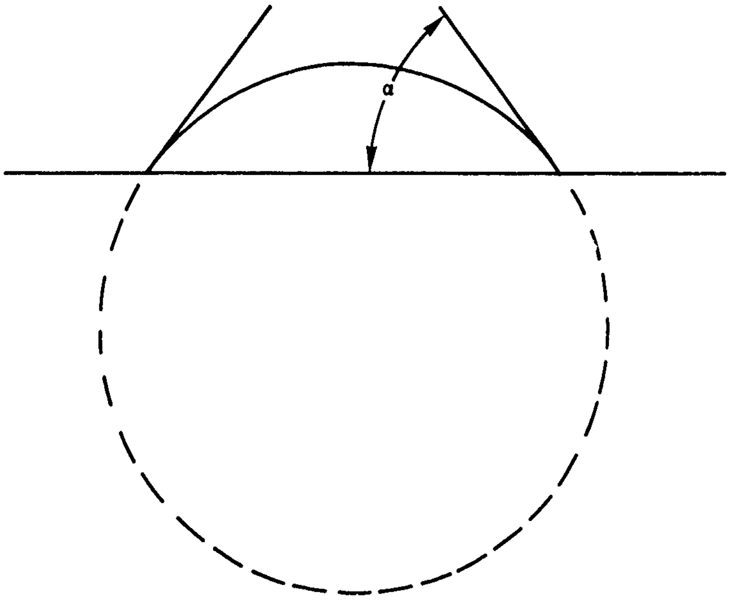

Fig. 1 — Profile and contact angle of a liquid drop on a solid surface and (including the dashed section of the circle) the profile of the drop's related imaginary sphere. The contact angle α of a liquid drop on a smooth, level solid surface is determined by the chemical and physical characteristics of the material (mutual solubility and surface tension) at the interface. In general the contact angle of a given drop is larger on a low-energy surface and smaller on a high-energy surface. For clean metal surfaces, and other high-energy solids which are "wet" by most liquids, a drop approaches a zero contact angle, and the measurement of the contact angle can be a sensitive means for detecting a monolayer or less of low-surface-energy contamination on the solid, such as water and various organic materials.

porthole protusion on the chamber could be visually observed through the porthole cover and their contact angles measured. The significance of this arrangement is that the sample did not have to be exposed to the laboratory atmosphere before the contact angle was measured. This takes on added significance in the following discussion of some of the experiments. All contact angle measurements, made after glow discharge cleaning, were made in the porthole with the pure nitrogen atmosphere, unless otherwise specifically mentioned. All samples were prepared as described in Appendix C.

All the results are documented in the tables in Appendix D. Figures 2a through 2e summarize the results of the tests for specific operating conditions as stated in the figure titles. The lower limit of the contact angle, which is too small to measure, indicates a surface free of both water and of substances which are hydrophobic. The theory of the significance of the small contact angle is discussed in a number of papers by Zisman and associates [9-11] and others. For $I_2(CH_2)$, when $\alpha < 5^\circ$, there is less than a monomolecular layer of water on the surface, with the amount reducing as the angle reduces. A similar criterion holds for the contact angles of H_2O: a low $\alpha < 5^\circ$ indicates less than a monomolecular layer of hyrophobic substances such as paraffin, lubricating oils, pump oils, hydrocarbons, and halide carbons.

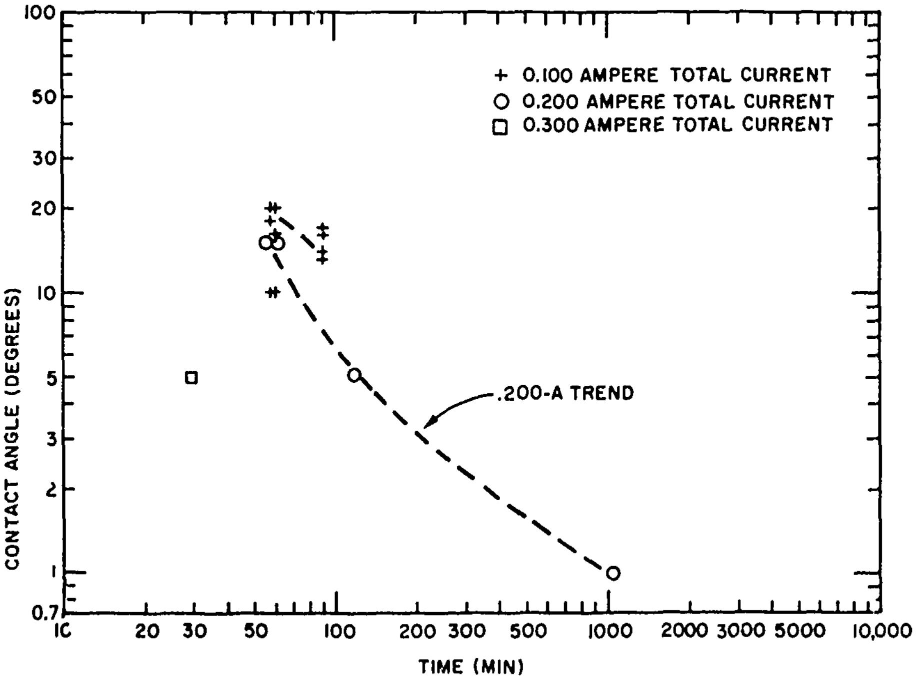

Fig. 2a — Contact angles of $I_2(CH_2)$ drops on ungrounded stainless-steel samples cleaned at 0.005 torr (in an argon flow) and a radial distance R from the anode at the center of the chamber of 38 cm. The values plotted are listed in Table D2.

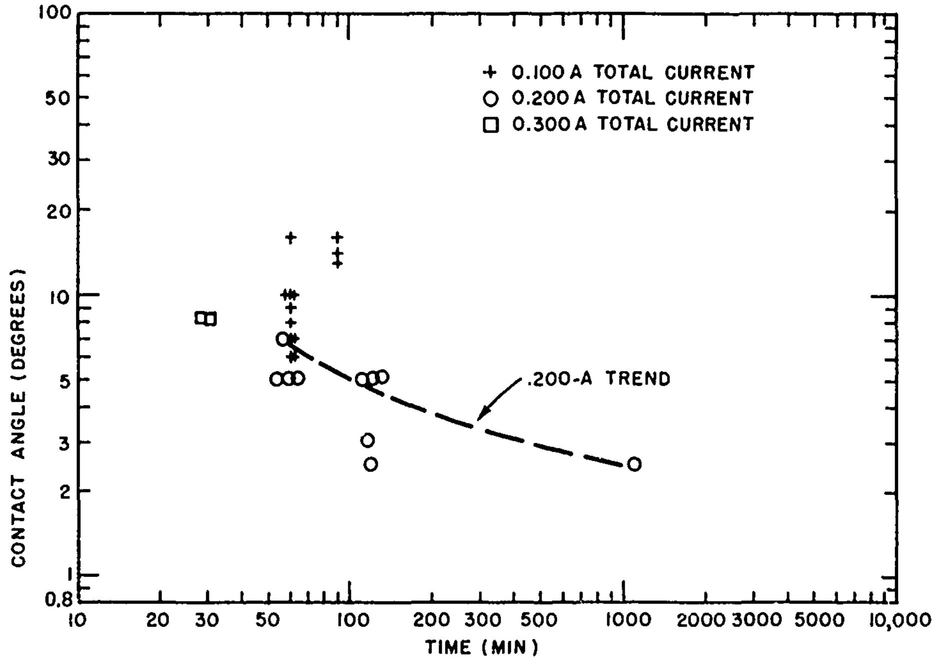

Fig. 2b — Contact angles of H_2O drops on ungrounded stainless-steel samples cleaned at 0.005 torr and a radial distance R of 38 cm. The values plotted are listed in Table D2.

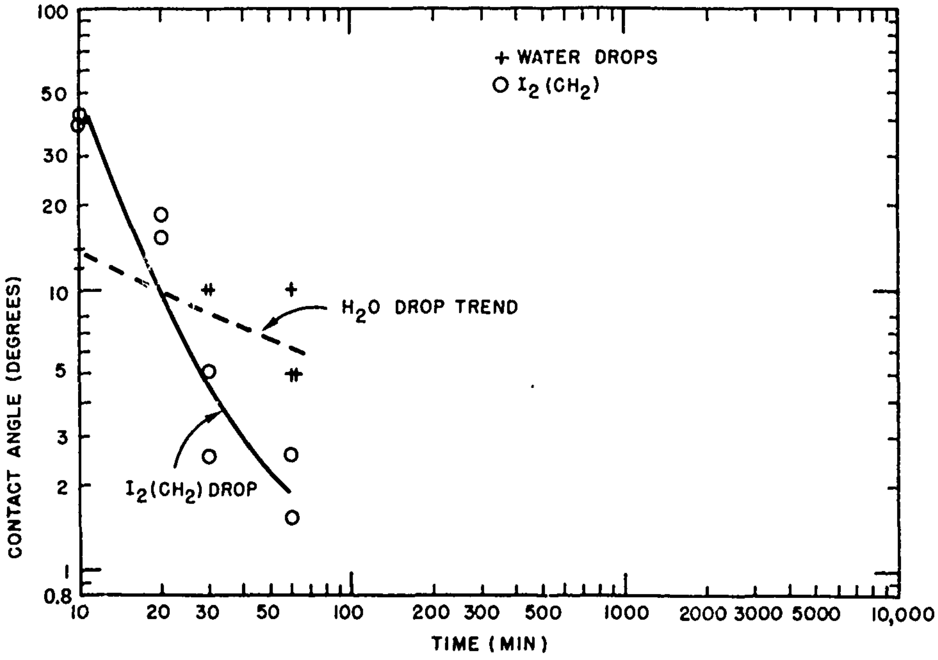

Fig. 2c — Contact angles of drops on grounded stainless-steel samples cleaned at 0.005 torr and a distance R of 18 cm using a total current of 0.300 A. The values plotted are listed in Tables D3a and D3b.

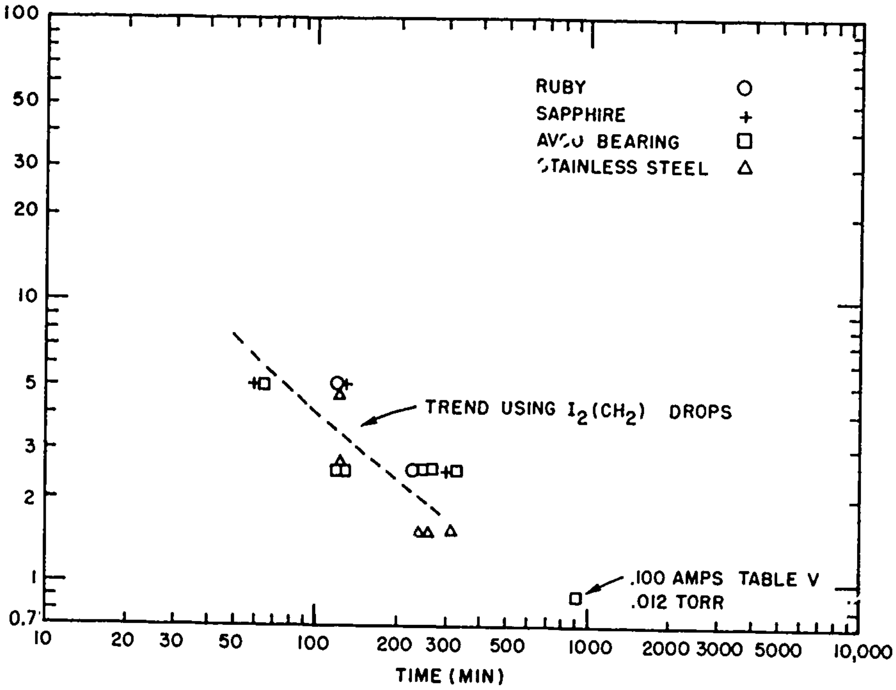

Fig. 2d — Contact angles of $I_2(CH_2)$ drops on ungrounded Al_2O_3 samples cleaned at 0.020 torr and a distance R of 18 cm using a total current of 0.200 A. The values are listed in Table D7 and (where indicated) Table D6a.

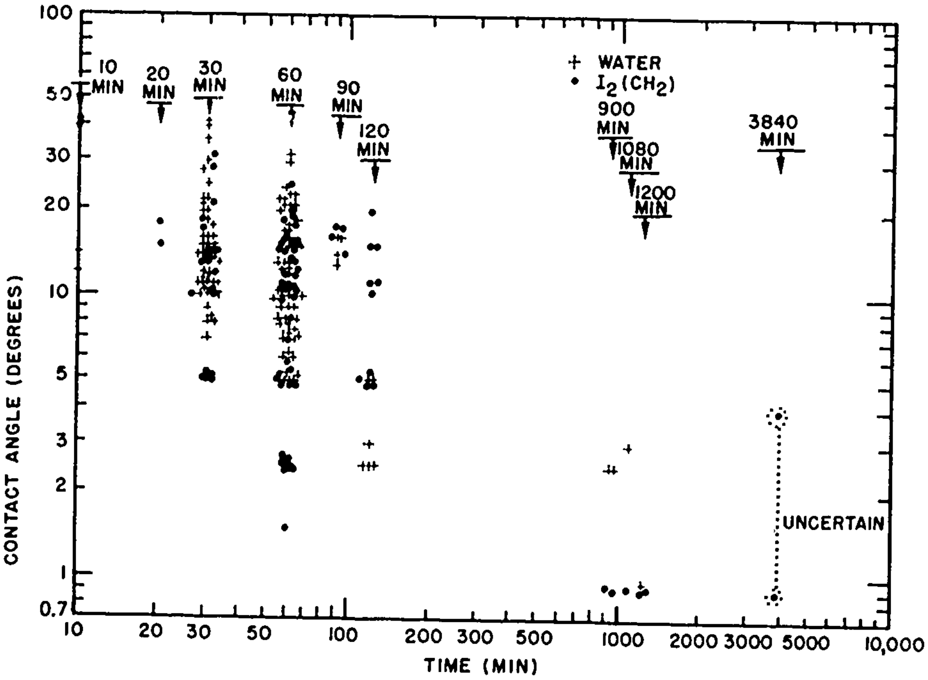

Fig. 2e — Composite plot of all data within the pressure range 0.002 to 0.200 torr and its related voltage range, the total-current range 0.100 to 0.400 A, and the distance-R range 18 to 38.7 cm. This plot indicates a trend toward increased cleanliness (decontamination) with time even though the conditions vary widely in the shorter time zones.

The starred point in the upper right of Fig. 2 may seem out of place. This is the result of a single experiment as follows: four samples were cleaned at one time by exposing them to the plasma for 60 minutes before the chamber was backfilled. Three samples were tested for cleanliness and showed contact angles of less than 10°. All four were left in the tank, which was pumped down again, and they were again plasma cleaned for 60 minutes; then the plasma was turned off, and the pumps were left running and the cleaning gas flowing for about 18 hours (overnight). The only difference from the cleaning mode was that the plasma was turned off. After the chamber was backfilled the following morning, the fourth sample was tested by contact-angle measurements and found to be more contaminated than it was before it had been put into the cleaning chamber (Table D4, run 13). The inference from this experiment is that the contamination was due to the continuous outgassing of the chamber in the low-pressure environment. In contrast to this another experiment was run in which, after the sample was cleaned for 60 minutes and then the chamber was backfilled, the cleaned sample was allowed to stay in the chamber overnight at a pressure slightly above 1 atmosphere. In this case the contact angles measured (Table D3, run 4) the same low angles measured on other samples immediately after the backfilling.

The implication from this test is that at 1 atmosphere pressure the outgassing of impurities from the chamber during about 18 hours is too low for the recontamination to be significant. This low recontamination rate also suggests the possibility of working with superclean materials and conducting assembly operations without fear of significant recontamination of the parts from the other materials in an environment, such as in a glove box.

A third experiment is illustrated in Fig. 3. Four samples were cleaned overnight, one was tested in the chamber before removing it from the porthole, and then all four samples were removed (Table D2, run 9). The second sample was tested by $I_2(CH_2)$ drop and a water drop after a 10-minute exposure to air (at 65°F and with a measured relative humidity of 40%). The contact angle α of the $I_2(CH_2)$ droplet was back to where it was before the cleaning process and remained essentially the same for the following 3-hour and 6-hour time intervals. This indicates that immediately on exposure to the air of the room the surface was recontaminated with water film of the original order of magnitude, almost as if it had never been cleaned. The water drop however indicated a much lower rate of accumulation of hydrophobic substances on the clean surface, or on the water film already covering the surface. The different contamination rates are directly related to the relative amounts of the different amounts of contaminants available and on the existance of an ultimate state of equilibrium between the contamination density in the air and on the surface.

Figure 4 illustrates a series of experiments showing the contact angle as a function of the pressure, with the other controllable variables kept constant. These data show a trend toward more efficient cleaning at lower pressures. Since the current and time interval is the same for all pressures, then the total number of ion impacts must be unchanged; therefore the measured cleaning efficiency lies in the average increase in the amount energy imparted to the ions over the greater length of the mean free paths in the lower pressure regimes. This reasoning leads to further speculation that the combination of field-strength and mean-free-path control can lead to calculating the minimum conditions required for cleaning any surface when the bonding energies between the contaminants and the surface is known.

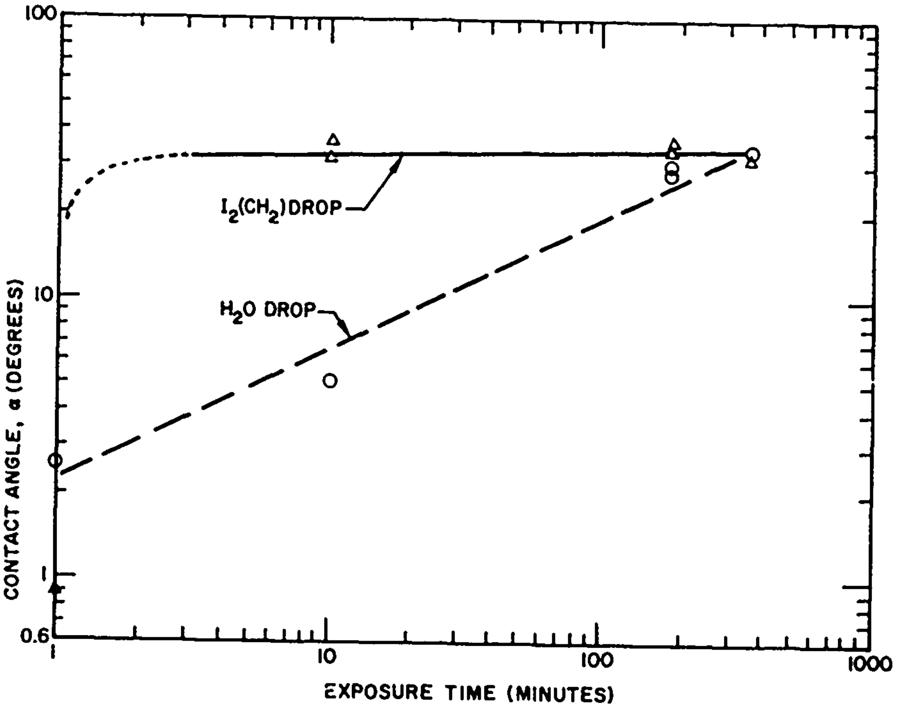

Fig. 3 — Recontamination of cleaned samples by air after removal from the chamber

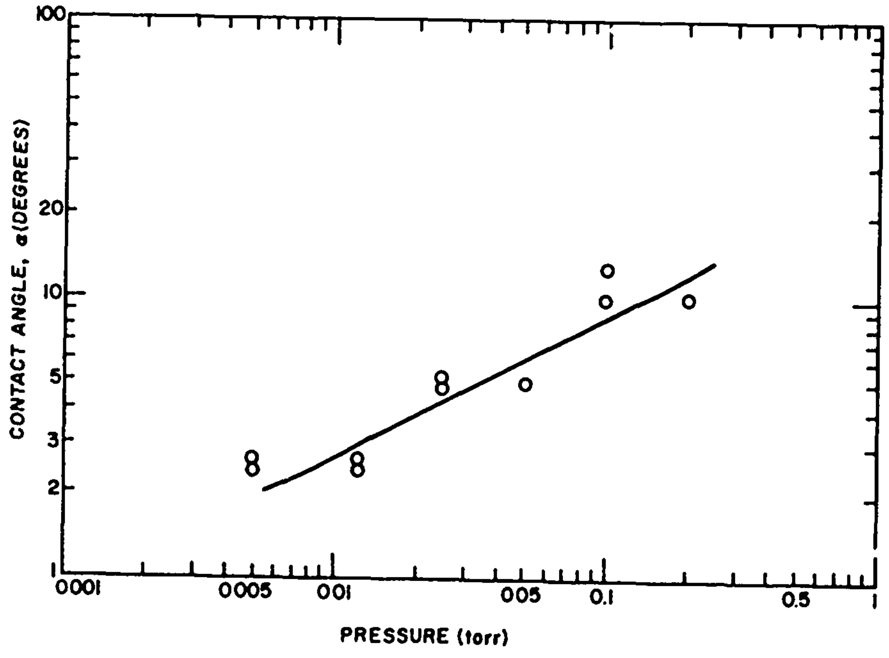

Fig. 4 — Contact angle after 60 minutes with a current of 0.100 A as a function of pressure, showing the influence of the glow-discharge pressure on the cleaning of the samples. (The data plotted are listed in Table D3a.)

The data from cleaning stainless-steel samples, whether obtained when electrically grounding them or when isolating them, showed no significant difference in cleaning quality, perhaps because the contact angles were all so small that any significance was buried in the gross differences between samples.

The effect of varying the position of the samples relative to the center electrode was similarly inconclusive. It was hoped that since the cylindrical field is stronger at its center than at the cylinder wall, greater current density and the higher ion energy near the center electrode would result in better cleaning and subsequently lower contact angles. However, although there may be a trend to substantiate these hopes, the data are not precise enough to support a position-effect hypothesis.

Similarly the effect of varying the current while keeping all other parameters unchanged did not result in significant or systematic reduction of the contact angle. Again this may be because the angles were already so small that the differences were hidden by the gross uncertainties such as the differences between samples evident from the data obtained prior to the plasma cleaning measurements. Even after preparing all the stainless-steel samples the same way in the same wash water and the same rinse water, there were differences in contact angles not only between samples but from one area to another of the same sample—not great differences, but measurable ones.

CONCLUSIONS

The main conclusion reached in this report is that a continuous flow of inert gas through a glow-discharge cleaning chamber results in test surfaces on which the contamination is significantly lower than on test surfaces cleaned in a chamber without the continuous gas flow. The contaminants appear to be simply swept out of the cleaning chamber before they can recontaminate the surfaces of the chamber or the samples.

A more sophisticated statement is that the continuous flow of clean inert gas reduces the saturation level of contaminants in the chamber until the probability of recombination of the contaminant with the surface approaches zero. A simple analogy is the superiority of a vacuum sweeper over a broom.

A trend is observed toward higher cleaning efficiencies at lower pressures, which supports the idea that the resulting increase in the mean free path of the ion allows it to accumulate more kinetic energy before impact. This trend is somewhat tempered by the related observation that the greater mean free path may also increase the probability of recontamination of the cleaned sample and the chamber walls; before the contaminants are removed from the cleaning chamber by the mass flow action of the gas. The mass flow of the gas can be effective in sweeping out the contaminants only if the mean free paths are short compared with the dimensions of the chamber. Hence the higher energy of the ions, which increase the probability of outgassing and decontaminating the surfaces exposed to them must be balanced by a sufficient number of mean free paths in the chamber to allow the gas flow to effectively remove them from the cleaning chamber. Also the bombardment frequency (current density) must be low enough so as to not heat the sample so much as to change its surface characteristics. Nor can the ions be so energetic as to sputter off the surface material along with the contamination, since such a result is not compatable with the purpose of this experiment and has thus been deliberately avoided.

Thus the philosophy justifies a low-energy glow-discharge experiment as reported here.

ACKNOWLEDGMENTS

Thanks are due to Mr. J. Brown, Associate Superintendent, Plasma Physics Division, for his interest in, sense of responsibility for, and support of this project, to Elaine Shafrin of the Chemistry Division for the generous contribution of time spent in clarifying the relationship of contact angles to contamination levels on high-energy surfaces and for showing the techniques required for making reliable contact-angle measurements, to friends and associates who helped as well as advised on photographic problems, vacuum techniques, and general scientific and engineering support, and to Paul Carrol and the Machine Shop for fabricating critically important hardware (such as the sample holder) from imprecise drawings.

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Appendix A
THE VACUUM SYSTEM AND INSTRUMENTATION

The vacuum system consists of a Stokes microvac Model 212-H forepump (Fig. A1) with a manufacturers rated pumping speed of 4000 liters/min (140 cu ft/min). It is connected to a jet pump (an Edwards vapor booster pump Model 94G) with a manufacturers rated pumping speed of 2800 liters/s. The two pumps are connected through a 10-cm gate valve, a 2.5-m-long 5-cm-diameter flexible pipe, and the jet-pump exit baffle, with a net conductance of about 340 liters/min at the jet pump exit to the baffle (assuming the Stokes forepump will pump 4000 liters/min at the pump entrance). Due to the architectural limitations of the assigned laboratory space, the connecting pipe to the elbow cold trap is an S-shaped pipe, 25 cm in diameter with an effective length of a complete 38-cm-centerline-radius toroid, plus a 125-cm straight pipe and a 25-cm-diameter gate valve, an equivalent of about 3 m. The cold trap is a 110-cm-high by 110-cm-long elbow, with an 80-cm inside diameter, and is equipped with both a chevron-type Freon-colled baffle and a pair of spherical liquid-nitrogen baffles. The cold trap is connected directly to the main vacuum chamber or cleaning chamber, which is a 3/2-cm-long cylinder, with an 80-cm inside diameter and closed by a removable plate at the other end.

A center electrode is suspended in the center of the cylinder which is insulated at both ends and is just short enough so that the respective ends are further away from the end plate and the cold trap than from the cylinder wall. The end plate has ports on it for the working gas and for the clean gas used to backfill the chamber. Mounted on the back plate are a leak valve for the working gas and a cooling coil for freezing out any possible moisture in the backfill gas (N_2) plus a heating coil to heat the backfill gas again before it is expanded into the chamber.

Along the side of the chamber is a 30-cm-diameter porthole about 18 cm deep which serves as the experiment working space. The chamber has an 8-cm-diameter observation port on the top of the porthole and a small 2.5-cm-diameter access hole (45° around toward the right side-facing the porthole). Three other access cans are along the side of the chamber for attaching instrumentation and the electrical input to the center electrode.

The instrumentation is the flowmeter to the controlled leak valve, an Alphatron vacuum gauge, and a homemade manometer to assure that a positive pressure is reached before the small access hole is opened (to reduce probabilities of atmospheric contamination). A voltmeter and an ammeter is used to measure the total current through the sample. The dc power supply is a Regatron Model 222A with an output limited from 0 to 500 ma and 0 to 1000 V.

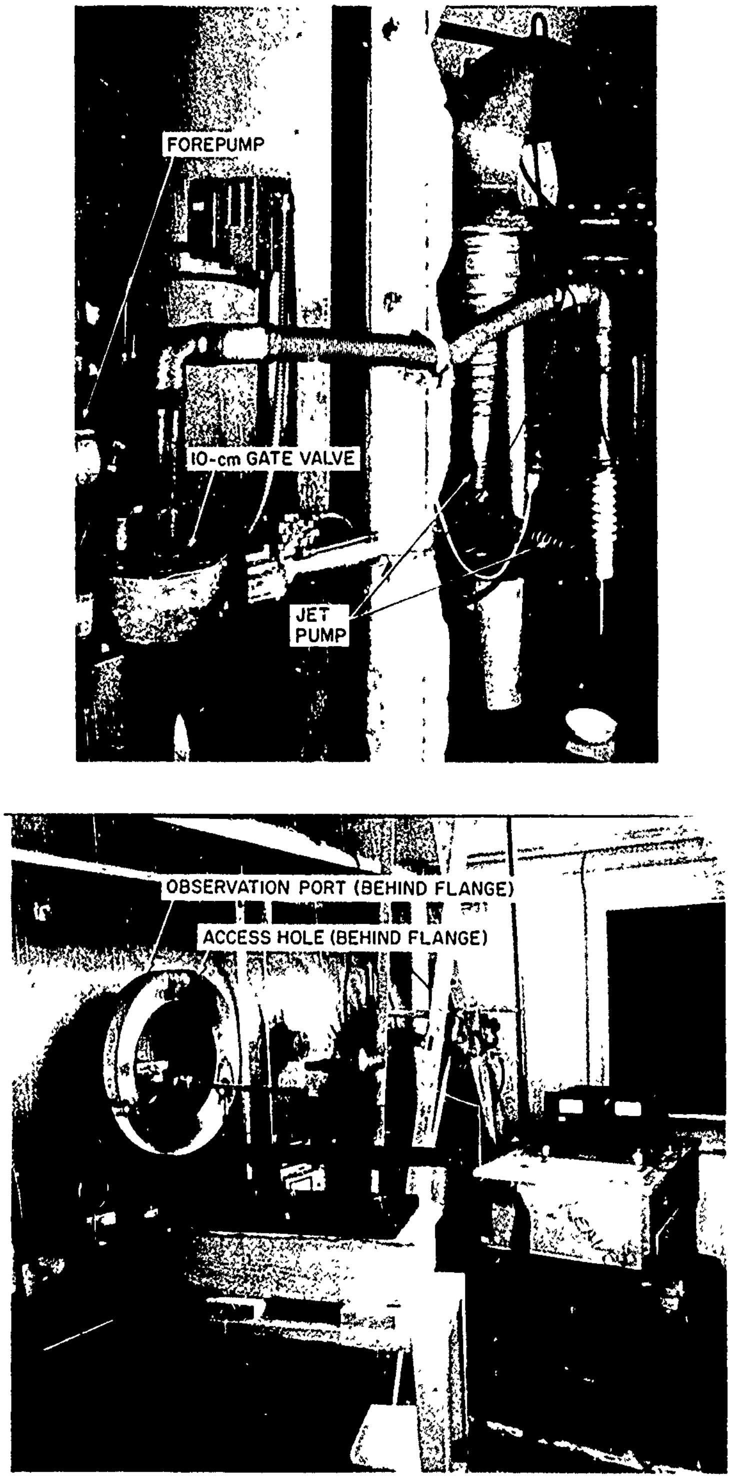
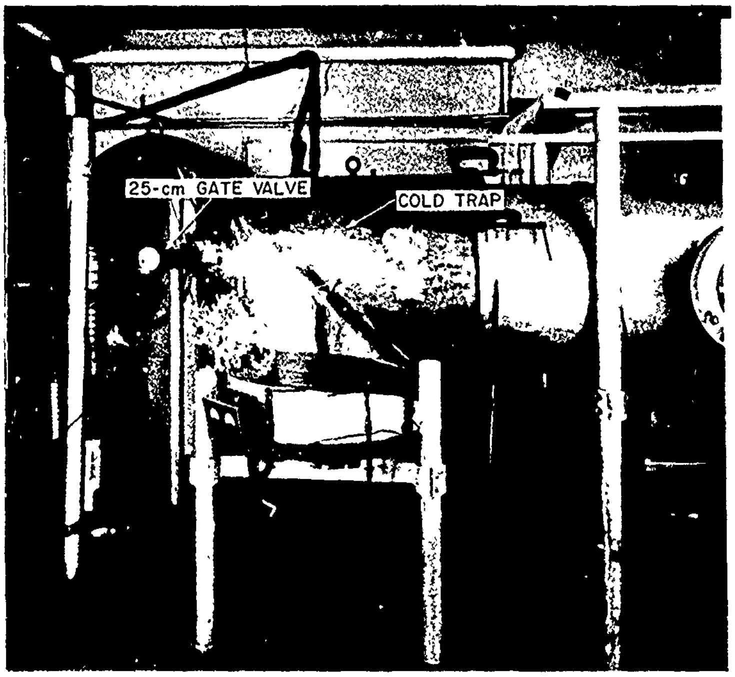


Fig. A1 — Vacuum system and instrumentation



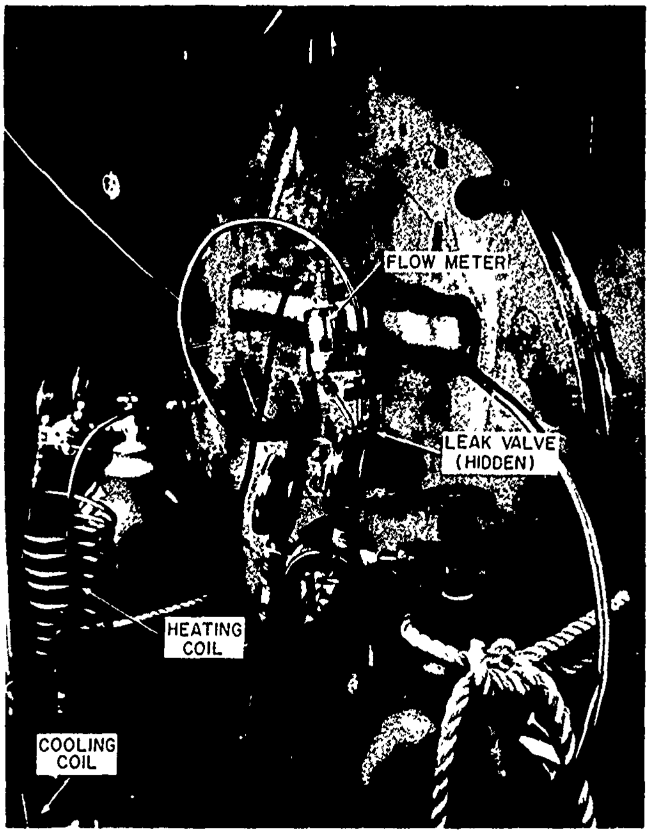


Fig. A1 — Vacuum system and instrumentation — (Continued)

Appendix B
THE CLEANING SYSTEM AND ITS CHARACTERISTIC VALUES

The forepump is a Stokes Model 212-H microvac pump. It is rated by the manufacturer to have a 4000 liter/min capacity at 1 atmosphere, which reduces to about 1700 liters/min at 0.100 torr. It is further reduced by the conductance through the connecting pipes to about 310 liters/min (by calculation) at the output of the Edwards Speedivac Model 94B. The Model 94B is rated at 2800 liters/s by the manufacturer and reduces to about 2750 liters/s by conductance to the cold trap.

Regardless of the manufacturers' claims, the system pumping performance is illustrated in Fig. B1 as it responded to a number of tests. Thus for example, to maintain a pressure of 0.100 torr, the use of the Stokes pump alone pumps about 9 cm^3 of standard-atmosphere argon per minute through the controlled leak valve, which expands to about

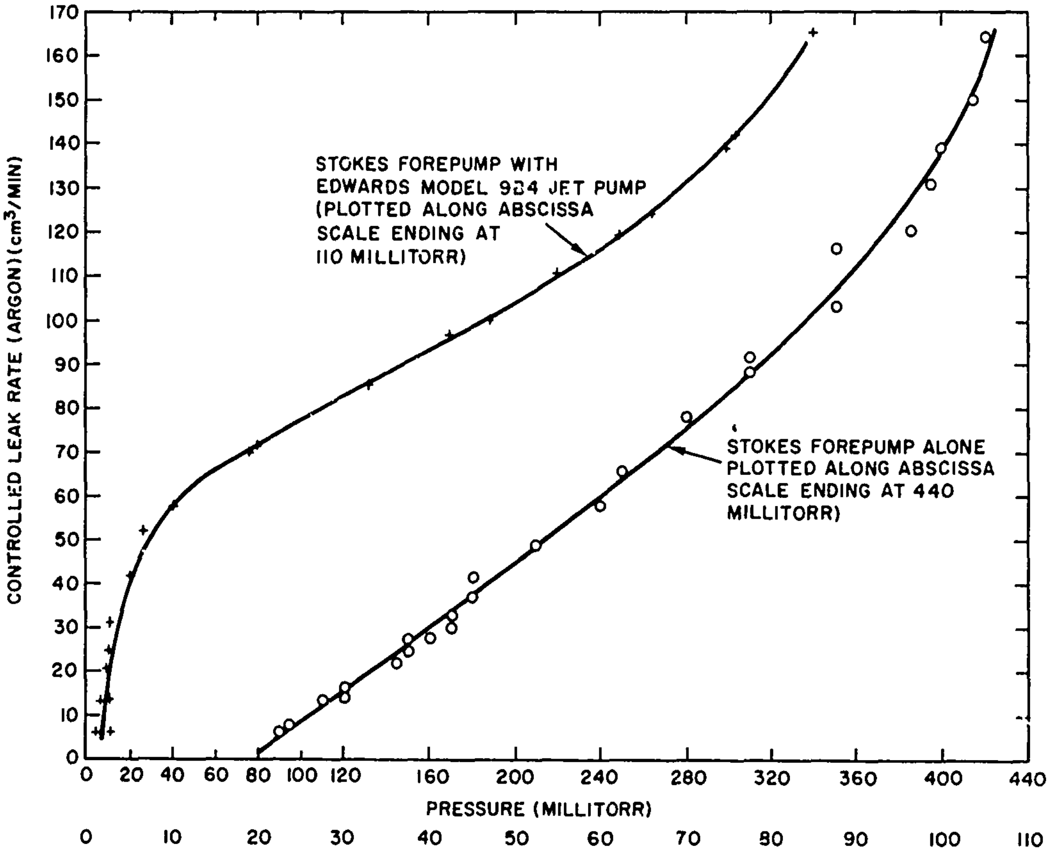


Fig. B1 — Measured effective pumping rates

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68 liters/min as a pumping rate through the entire system. However, when the jet pump is active in the pumping system, the gas flow rate is off the scale of the flowmeter to maintain the 0.100-torr pressure, but at 0.080 torr the controlled leak valve meters a flow of 150 cm^3/min, which expands to about 1400 liters/min. At lower pressures, down to 0.005 torr, the flow rate increases dramatically.

The volume of the chamber is about 1590 liters, and the rest of the system through the cold trap and connecting pipes to the 25-cm gate valve is about 650 liters more, for a total of 2240 liters. Final tests of the system's leak and outgassing rates with the gate valve closed showed that the pressure increase was about 0.001 torr per hour. This is the equivalent of 2240 microtorr-liters per hour, or 0.62 microtorr-liters/s, which is the equivalent of 0.817 mm^3/s of gas at one standard atmosphere. This leak rate is insignificant compared with the controlled leak rate for the operating system.

The inert gas used for glow-discharge cleaning was ultrapure argon purchased from the local source, the Southern Oxygen Division of the Air Products Company. The gas passes through a Granville-Phillips variable leak valve (Series 203) and then a Matheson flowmeter Model LF-100 into the inlet on the back plate of the chamber. The manufacturer's calibration correction curve for argon flow instead of air flow was used for all flow rates.

The surface of the cleaning cylinder, including the end plate but not the cold trap is about 82,850 cm^2, which yields an average current density of about 12 $\mu A/cm^2$ per ampere of total current. If the inside area of the cold trap is included, the total inside area is about 110,000 cm^2, or about 33% more. The glow discharge frequently appears to jump into the cold-trap cavity and then go out. When this happens, the current at the power supply jumps about 25 to 30%, just about enough to account for the increased area if the surface current density remains the same. No further investigation was made of the phenomena.

It was assumed for the purpose of this experiment that the volume density of the ionized particles in this glow discharge was so low that the static electric field of a cylindrical configuration would be essentially undisturbed. Figure B2 illustrates the field strength, normalized to the electrode voltage (V_0), as a function of distance from the center electrode, and was used to estimate the energy gain by a singly charged particle (ion) in the course of moving undisturbed through 1 mean free path length. This also assumes that the ion starts at rest or with the average kinetic energy of a particle at room temperature (which is rather insignificant compared to 1 electron-volt).

Figure B3 illustrates the results of measurements of the current and voltage required to maintain a glow discharge as a function of pressure. The anode voltage V_0 is the estimated center electrode voltage resulting from

$$V_0 = V_p I_p R,$$

where V_p is the voltage output of the power supply, I_p is the current output of the power supply, and I_pR is the resulting voltage drop across a standard 970-ohm resistance in the circuit. The chamber walls are the cathode and are at ground potential. The anode is at the center, so that the ion acceleration is essentially outward and perpendicular to the mass movement of the gas flow.

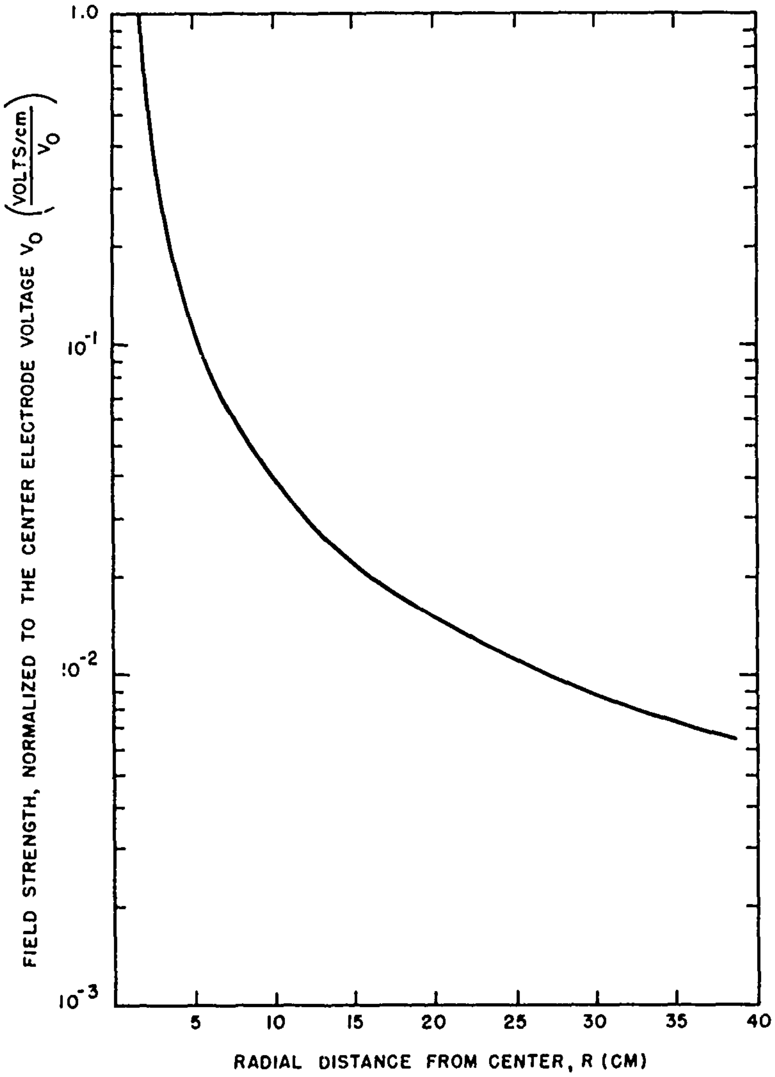


Fig. B2 — Assumed cylindrical field strength, normalized to the electrode voltage, as a function of the radius

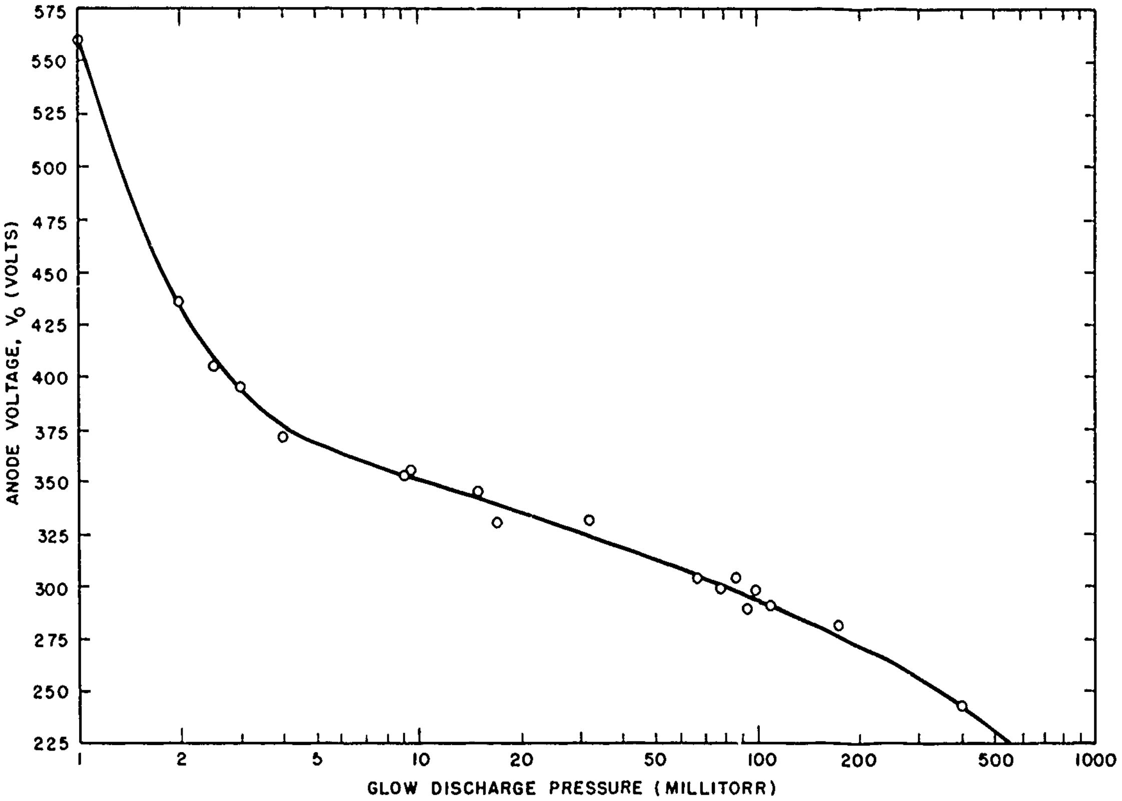


Fig. B3 — Minimum anode voltage required to maintain a glow discharge as a function of pressure

The dc power supply is a Regitron Model 222A. It delivers current over the range of 0 to 500 mA at voltages ranging from 0 to 1000 V. It is connected in series through a wire-wound resistor rated at 973 ohms to the center electrode. No attempt was made to calibrate resistance as a function of temperature, because the currents used were usually small enough so that the resistor did not get too hot to hold.

The backfilling gas, used to bring the chamber pressure back to slightly above 1 atmosphere was ultrapure nitrogen purchased from the same course as the argon: the Southern Oxygen Division of the Air Products Company. The nitrogen was passed through a coil immersed in a dry ice and acetone slurry so as to freeze out any contaminants which might be present and then was passed through a second coil, where it was heated to about room temperature before expanding into the chamber.

Appendix C
GLOW-DISCHARGE CLEANING OPERATION

CHEMICAL CLEANING AND PREPARATION OF SAMPLES FOR THE GLOW-DISCHARGE EXPOSURE

Except for some preliminary data (Table D1) all 16 stainless-steel samples were given a mirror polish such that all scratches were removed. After they were polished, they were soaked overnight in a 10% sodium hydroxide mixture and then rinsed and washed in a solution of Sparkleen and distilled water. The 16 pieces were rinsed as a group in three changes of distilled water and once in 2-propanol. Then they were air dried. The purpose in preparing the samples in this way was to let all the samples share all sources of possible contamination at the same time. For all subsequent prepartions the sodium hydroxide was not used.

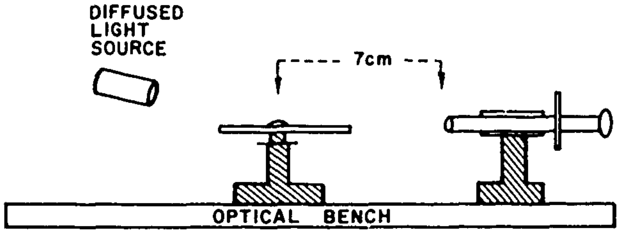
The aluminum oxide samples included two alumina gyro bearings from Avco, two artificial sapphire chips, and two ruby chips. These were cleaned with only the Sparkleen wash and distilled water rinses, since the alumina might chemically react with the sodium hydroxide and be destroyed.

CONTACT-ANGLE MEASUREMENTS

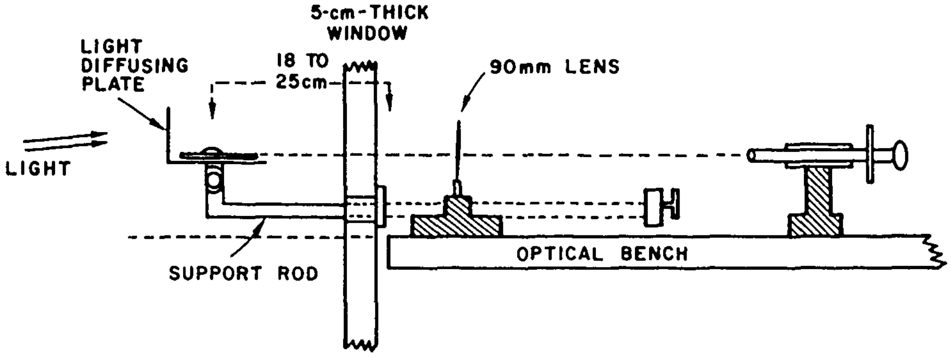
All samples were tested by measuring the contact angle of a drop of methylene oxide on one corner, and a drop of triply distilled water on another corner before being placed in the cleaning chamber for glow-discharge exposure.

After glow-discharge cleaning, all contact angles were measured through the observation window before the sample was exposed to the laboratory atmosphere. This measurement technique requires a modification of the goniometer optics so as to make it possible to see the objects inside of the porthole and is best described by the two examples in Fig. C1.

Figure C1a is the standard setup, with the drop about 6 to 7 cm from the object lens of the gonimeter. This setup is used to measure the precleaning contact angles. Figure C1b is the modified setup required to see through the window to the sample. There are not insurmountable difficulties with this, but the image of the drop is degraded. The angle measurements are reproducable to ±1° down to about 6° or 7°. They become uncertain below 5°, depending on the quality of the image, which is sometimes good but more often poor, depending on the placement of the optical system and the limited time required to make the optimum adjustment.



(a) Sample and drop outside the chamber



(b) Sample and drop inside the chamber

Fig. C1 — Optical arrangements for measuring contact angles

PUMPDOWN, GAS FLOW, AND GLOW DISCHARGE

After the vacuum system has been closed and checked against a checkoff list, the forepump is turned on and allowed to pump down to about 1 torr before the cold-trap refrigeration unit and jet-pump heater are turned on. This keeps most of the humidity from clogging up the chevron baffles, which could reduce the conductivity of the vacuum system. After the pressure has stabilized at about 0.0005 to 0.0010 torr, the controlled leak is opened and the pressure builds up to the desired pressure and is allowed to stabilize before the power is turned on for the glow discharge. When the glow discharge is first turned on, the gas flow needs continual adjustments for about 10 minutes to maintain a constant pressure, after which it settles down to a rather constant flow.

For subsequent starts the cold-trap refrigeration is on all the time, because the backfilling gas is dry, and because it keeps recontamination of the system from the cold trap to a minimum. Also the 25-cm gate valve is closed for the backfilling operation so the heater to the jetpump is turned off and allowed to cool until it is about time to restart. At that time the forepump is turned off and air is bled into the pumping side of the 25-cm gate valve to equalize the pressure before opening it for the next start. For subsequent starts the forepump and the jet-pump heater are turned on at the same time.

The gas flow is always turned on after the pumping system has stabilized at its lowest pressure (somewhere between 0.0005 and 0.0010 torr, depending on its mood) so as to build the pressure up to the desired level in a minimum time. Letting the pumping system first reach stabilization also assures that most of the gas in the chamber is argon, since the pumping system has literally swept out the remaining gaseous residues such as nitrogen, oxygen, and water vapor.

Argon is used because it is the cheapest chamically inert gas available (ionized nitrogen is chemically active) and because as an ionized ballistic missile it has enough mass to dislodge hydrocarbon and water-molecule forms of surface contamination. Particle contamination, such as dust, will probably not be disturbed, so the only consideration given to particles is to those which are not removed by the preparation process; they remain to be cleaned by the glow-discharge process.

The glow discharge was operated between 0.002 torr and 0.2 torr, and at currents between 0.100 and 0.400 A, with whatever voltage was required. It was turned on after the pressure and gas flow was stabilized and turned off at the end of a predetermined time interval. It was mentioned in Appendix B that the average current to the walls of the chamber were 12 μA/cm^2 per ampere; however this does not hold true for the samples which were not attached to the wall but were suspended into the chamber. For example, Figure. C2 shows the verification of the average current through a 6.5-cm^2 sample at 18 cm from the anode and how it changes with total current and with pressure. These samples were connected to ground through a sensitive ammeter. The experimental data, obtained between January 10 and January 15, 1975, is given in Appendix D (Tables D3).

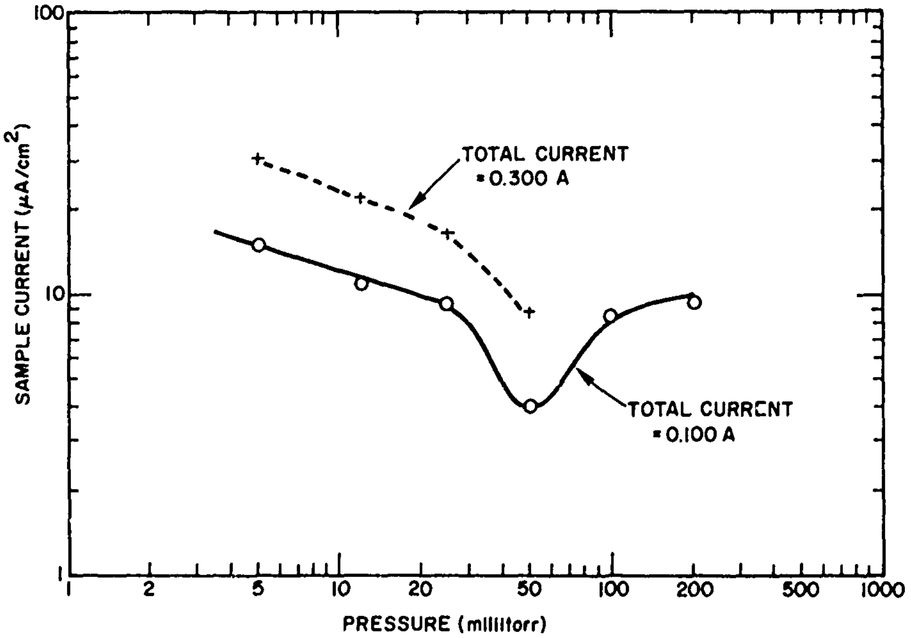


Fig. C2 — Sample current at constant total current as a function of pressure

After the cleaning time is over, the chamber is immediately backfilled with clean dry nitrogen gas to a pressure slightly above 1 atmosphere. When the small access hole or the side of the porthole is opened to put a test drop on one of the samples, the greater pressure on the inside reduces the probabilities of contamination from the laboratory atmosphere before the contact angles are measured. It turned out, as one of the experiments show, that after a sample sat in the backfilled chamber for 16 hours (overnight), the measured contact angles were comparable with those obtained immediately after backfilling was completed. Thus slight delays probably do not influence the results.

Appendix D
DATA AND COMMENTS

The data in Tables D1 through D7 are listed as originally recorded. This is a record of the effort to identify the comparative absence of contamination on certain select surfaces of stainless steel, except for Al_2O_3 at the last in the forms of sapphire, ruby, and ceramic. During the experiments it was decided that some items were of little value and some procedures were not productive, and then again that something missing from the early observations needed to be included. It was discovered early that putting a drop of methylene iodide on one side of a sample and a drop of water on the other side of the same sample did not seem to change the size of the contact angle of either drop regardless of which one was put on first, except in the case of spontaneous spreading, in which case no attempt was made to put two drops on one sample. However putting two drops on one sample otherwise made twice as many observations possible. The ritual was to put the methylene iodide on first, since it had a higher density and a lower vapor pressure.

The first few runs were exploratory; they tested out the upper and lower limits of the pressure and energy and tried out the results with an α-bromonapthalene drop. It was decided during these experiments to use only methylene iodide to detect water films, since $I_2(CH_2)$ is highly hydrophobic and has a high surface tension, and to use water to detect hydrophobic films. Contamination present on the surface, after otherwise careful cleaning of particulate matter, should be mostly attributable to contaminants present in the air and the cleaning solutions themselves, such as soap film, water, human breath residues, and body odor. Perhaps their presence could not be identified, but their absence could be.

Table D1 — Series—I Glow-Discharge-Cleaning Data: Contact Angles of Drops on Ungrounded Stainless-Steel Samples on a Stainless-Steel Holder

Sample Number	Exposure Time (min)	Total Current (A)	Average Current* ($\mu A/cm^2$)	Gas	Pressure (torr)	Contact Angle, α (deg)				Remarks
						H_2O		$I_2(CH_2)$		
						Left	Right	Left	Right	
Run 1 — Unpolished samples outside the chamber in air and then inside the chamber in argon at a radial distance R from the center electrode = 38.7 cm (wall distance). This run was over a weekend to glow-discharge clean the system. The samples were washed only with soap and water and rinsed with distilled water.										
1	0	0	0	Air	760	—	—	35	34	—
2	0	0	0	Air	760	84	85	—	—	—
1	60	0.100	1.2	Argon	0.200	—	—	17	18	—
2	3840	0.100	1.2	Argon	0.200	—	—	?	?	$I_2(CH_2)$ too thin to measure
3	3840	0.100	1.2	Argon	0.200	—	—	4	6	—
4	3840	0.100	1.2	Argon	0.200	—	—	?	?	$I_2(CH_2)$ too thin to measure
Run 2 — Unpolished samples, at R = 38.7 cm when in the chamber. The chemical cleaning procedure of Appendix C was used.										
1	0	0	0	Air	760	—	—	35	42	—
4	0	0	0	Air	760	85	80	—	—	—
1	30	0.200	2.4	Argon	0.020	?	<4	—	—	Reflections obscured the left side of the drop profile
2	30	0.200	2.4	Argon	0.020	—	—	?	9	
3	30	0.200	2.4	Argon	0.020	—	—	?	14	
4	30	0.200	2.4	Argon	0.020	?	<4	—	—	
Run 3 — Newly polished samples with no precleaning, at R = 38.7 cm when in the chamber.										
1	0	0	0	Air	760	110	105	—	—	—
2	0	0	0	Air	760	108	108	—	—	—
3	0	0	0	Air	760	—	—	38	39	α — Bromonaphalene instead of $I_2(CH_2)$.
4	0	0	0	Air	760	—	—	35	40	
1	180	0.100	1.2	Argon	0.005	—	—	?	?	α—Bromonaphalene, too thin to measure
2	180	0.100	1.2	Argon	0.005	—	—	?	?	
3	180	0.100	1.2	Argon	0.005	40	?	—	—	Reflections obscured the right side of the drop
4	180	0.100	1.2	Argon	0.005	35	?	—	—	

*Averaged over the inside area of the chamber.

Table continues

Table D1 (Continued) — Series—I Glow-Discharge-Cleaning Data: Contact Angles of Drops on Ungrounded Stainless-Steel Samples on a Stainless-Steel Holder

Sample Number	Exposure Time (min)	Total Current (A)	Average Current ($\mu A/cm^2$)	Gas	Pressure (torr)	Contact Angle, α (deg)				Remarks
						H_2O		$I_2(CH_2)$		
						Left	Right	Left	Right	
Run 4 — Polished Samples, at R = 38.7 cm when in the chamber										
1	0	0	0	Air	760	60	60	—	—	—
2	0	0	0	Air	760	70	70	—	—	—
3	0	0	0	Air	760	60	66	—	—	—
4	0	0	0	Air	760	45	45	—	—	—
1	1200	0.100	1.2	Argon	0.005	—	—	<1	<1	Overnight cleaning run ≈ 20 hr.
2	1200	0.100	1.2	Argon	0.005	—	—	<1	<1	
3	1200	0.100	1.2	Argon	0.005	<1	<1	—	—	spontaneous wetting.
4	1200	0.100	1.2	Argon	0.005	<1	<1	—	—	
Run 5 — Polished samples, at R = 28 cm. (Sample 1 was checked with an Auger Spectrometer with inconclusive results; nothing was found except stainless steel.) The contact angle α was estimated by the spreading ratio n using Eqs. (6) and (3c) of Appendix E.										
1	30	0.100	1.2	Argon	0.006	—	—	<5	<5	—*
2	30	0.100	1.2	Argon	0.006	—	—	<5	<5	The drop diameter spread from ≈ 1.5 mm to ≈ 7 mm in 30 s. Therefore n > 4.
3	30	0.100	1.2	Argon	0.006	—	—	<5	<5	
4	30	0.100	1.2	Argon	0.006	—	—	<5	<5	
Run 6 — A different set of polished samples, at R = 38.7 cm										
5	30	0.100	1.2	Argon	0.005	18	?	—	—	Reflections obscured the right side of the drop
6	30	0.100	1.2	Argon	0.005	22	?	—	—	
7	30	0.100	1.2	Argon	0.005	14	?	—	—	
8	30	0.100	1.2	Argon	0.005	30	?	—	—	
Run 7 — Polished samples, at R ≈ 35 cm										
1	30	0.100	1.2	Argon	0.005	12	12	—	—	n ≈ 3†
2	30	0.100	1.2	Argon	0.005	8	10	—	—	—
3	30	0.100	1.2	Argon	0.005	10	15	—	—	—
4	30	0.100	1.2	Argon	0.005	10	14	—	—	—

*This sample went to an Auger Spectrometer. The results were inconclusive; nothing was found except the expected components of stainless steel.

†The spreading ratio n ≈ 3 observed in supplementary to the direct measurement α = 12°. In the case of run 8, samples 1 through 3, for example, a direct measurement of α was not possible, and the value <10 listed is that determined by observing that n > 3.

Table Continues

Table D1 (Concluded) — Series–I Glow-Discharge-Cleaning Data: Contact Angles of Drops on Ungrounded Stainless-Steel Samples on a Stainless-Steel Holder

Sample Number	Exposure Time (min)	Total Current (A)	Average Current ($\mu A/cm^2$)	Gas	Pressure (torr)	Contact Angle, α (deg)				Remarks
						H_2O		$I_2(CH_2)$		
						Left	Right	Left	Right	
Run 8 — Polished samples, at R = 38 cm										
5	30	0.100	1.2	Argon	0.005	—	—	?	≲10	n > 3 ⇒ α < 10 Reflections obscured the left side.
6	30	0.100	1.2	Argon	0.005	—	—	?	≲10	
7	30	0.100	1.2	Argon	0.005	—	—	?	<10	
8	30	0.100	1.2	Argon	0.005	—	—	?	<5	n > 4 ⇒ α < 5. Reflections obscured left side.
Run 9 — Polished samples, at R = 38.7 cm										
1	30	0.070	0.85	Argon	0.002	—	—	30	?	Reflections obscured the right side.
2	30	0.070	0.85	Argon	0.002	—	—	34	?	
3	30	0.070	0.85	Argon	0.002	?	35	—	—	Reflections obscured the left side
4	30	0.070	0.85	Argon	0.002	?	22	—	—	

Sample No.	Expos. Time (min)	Current		Gas	Gas Flow Rate (cm^2/min)	Pressure (torr)	Contact Angle, α (deg)				Remarks
		Total (A)	Average ($\mu A/cm^2$)				H_2O		$I_2(CH_2)$		
							Left	Right	Left	Right	
Run 10 (5 Nov. 1974) — Polished samples, at R = 38 cm when in the chamber											
5	0	0	0	Air	—	760	—	—	?	?	No data, because photographs of the drops were underexposed.
6	0	0	0	Air	—	760	—	—	?	?	
7	0	0	0	Air	—	760	?	?	—	—	
8	0	0	0	Air	—	760	?	?	—	—	
5	30	0.100	1.2	Argon	34	0.006	—	—	≲10	≲10	n > 3. Reflections obscured the profile.
6	30	0.100	1.2	Argon	34	0.006	—	—	<10	<10	
7	30	0.100	1.2	Argon	34	0.006	—	—	≲5	≲5	n > 4. Reflections obscured the profiles.
8	30	0.100	1.2	Argon	34	0.006	—	—	<5	<5	
Run 11 — Polished samples, at R = 28 cm. The samples were not precleaned with NaOH or soap and water.											
9	30	0.100	1.2	Argon	36	0.006	36	?	28	?	Reflections obscured the right side.
10	30	0.100	1.2	Argon	36	0.006	42	?	31	?	
11	30	0.100	1.2	Argon	36	0.006	?	40	?	21	Reflections obscured the left side.
12	30	0.100	1.2	Argon	36	0.006	?	45	—	—	
Run 12 — Polished samples at R = 28 cm											
13	30	0.100	1.2	Argon	36	0.006	18	28	—	—	—
14	30	0.100	1.2	Argon	36	0.006	12	?	—	—	Reflections obscured right side.
15	30	0.100	1.2	Argon	36	0.006	—	—	≲10	≲10	n > 3.
16	30	0.100	1.2	Argon	36	0.006	—	—	<10	<10	

Table D2 — Series—II Glow-Discharge-Cleaning Data: Grounded Polished Stainless-Steel Samples on a Lucite Holder

Sample No.	Expos. Time (min)	Current		Gas	Gas Flow Rate (cm^3/min)	Pressure (torr)	Contact Angle, α (deg)				Remarks
		Total (A)	Average ($\mu A/cm^2$)				H_2O		$I_2(CH_2)$		
							Left	Right	Left	Right	
Run 1 (22 Nov. 1974) — Samples at R = 35 cm when in the chamber											
1	0	0	0	Air	0	760	70	70	—	—	—
2	0	0	0	Air	0	760	65	70	—	—	—
1	60	0.100	1.2	Argon	36	0.005	10	?	—	—	Reflections obscured right side.
2	60	0.100	1.2	Argon	36	0.005	10	12	—	—	—
3	60	0.100	1.2	Argon	36	0.005	16	?	—	—	Reflections obscured right side.
4	60	0.100	1.2	Argon	36	0.005	<10	<10	—	—	$n \geqslant 3 \Rightarrow \alpha < 10$.
Run 2 (5 Dec. 1974) — Samples at R = 38 cm when in the chamber											
5	0	0	0	Air	0	760	80	80	—	—	—
6	0	0	0	Air	0	760	90	85	—	—	—
7	0	0	0	Air	0	760	70	75	50	52	—
8	0	0	0	Air	0	760	75	75	48	48	—
5	90	0.100	1.2	Argon	34	0.005	16	?	17	?	—
6	90	0.100	1.2	Argon	34	0.005	16	14	16	13	—
7	90	0.100	1.2	Argon	34	0.005	?	13	14	?	—
8	90	0.100	1.2	Argon	34	0.005	—	—	17	?	—
Run 3 (9 Dec. 1974) — Samples at R = 38 cm											
9	60	0.100	1.2	Argon	?	0.002	12	17	11	12	—
10	60	0.100	1.2	Argon	?	0.002	15	18	6	7	—
11	60	0.100	1.2	Argon	?	0.002	13	23	12	10	—
12	60	0.100	1.2	Argon	?	0.002	15	21	25	?	Reflections obscured at right of $I_2(CH_2)$
Run 4 (10 Dec. 1974) — Samples at R = 38 cm when in chamber											
13	0	0	0	Air	0	760	27	30	—	—	—
14	0	0	0	Air	0	760	30	30	—	—	—
15	0	0	0	Air	0	760	43	37	—	—	—
16	0	0	0	Air	0	760	40	38	—	—	—
13	60	0.100	1.2	Argon	25	0.015	23	21	—	—	—
14	60	0.100	1.2	Argon	25	0.015	20	21	—	—	—
15	60	0.100	1.2	Argon	25	0.015	—	—	15	15	—
16	60	0.100	1.2	Argon	25	0.015	—	—	19	15	—

Table Continues

Table D2 (Continued) — Series—II Glow-Discharge-Cleaning Data: Grounded Polished Stainless-Steel Samples on a Lucite Holder

Sample No.	Expos. Time (min)	Current		Gas	Gas Flow Rate (cm^3/min)	Pressure (torr)	Contact Angle, α (deg)				Remarks
		Total (A)	Average ($\mu A/cm^2$)				H_2O		$I_2(CH_2)$		
							Left	Right	Left	Right	
Run 5 (11 Dec. 1974) — Samples at R = 18 cm											
1	60	0.200	2.4	Argon	24	0.006	—	—	15	15	—
2	60	0.200	2.4	Argon	24	0.006	—	—	18	15	—
3	60	0.200	2.4	Argon	24	0.006	5	5	—	—	—
4	60	0.200	2.4	Argon	24	0.006	5	7	—	—	—
Run 6 (11 Dec. 1974) — Samples at R = 38 cm when in the chamber											
5	0	0	0	Air	0	760	20	23	—	—	—
6	0	0	0	Air	0	760	20	22	—	—	—
7	0	0	0	Air	0	760	22	20	—	—	—
8	0	0	0	Air	0	760	22	25	—	—	—
5	120	0.200	2.4	Argon	24	0.006	<5	<5	11	10	—
6	120	0.200	2.4	Argon	24	0.006	—	—	15	20	—
7	120	0.200	2.4	Argon	24	0.006	$\lesssim 5$	$\lesssim 5$	—	—	$n \gtrsim 4 \Rightarrow \alpha \lesssim 5.$
8	120	0.200	2.4	Argon	24	0.006	<5	<5	15	11	$n \gtrsim 4 \Rightarrow \alpha < 5.$
Run 7 (12 Dec. 1974) — Samples at 38 cm when in the chamber											
9	0	0	0	Air	0	760	85	88	—	—	—
10	0	0	0	Air	0	760	86	88	—	—	—
11	0	0	0	Air	0	760	—	—	38	38	—
12	0	0	0	Air	0	760	—	—	38	38	—
9	120	0.200	2.4	Argon	24	0.005	—	—	$\lesssim 5$	$\lesssim 5$	Photographs not good enough; too many reflections.
10	120	0.200	2.4	Argon	24	0.005	—	—	$\lesssim 5$	$\lesssim 5$	
11	120	0.200	2.4	Argon	24	0.005	$\lesssim 3$	$\lesssim 3$	—	—	
12	120	0.200	2.4	Argon	24	0.005	<3	<3	—	—	
Run 8 (12 Dec. 1974) — Samples at R = 28 cm when in the chamber											
1	0	0	0	Air	0	760	—	—	30	30	—
2	0	0	0	Air	0	760	—	—	30	31	—
3	0	0	0	Air	0	760	54	53	—	—	—
4	0	0	0	Air	0	760	63	63	—	—	—
1	120	0.200	2.4	Argon	24	0.005	$\lesssim 2.5$	$\lesssim 2.5$	—	—	$n > 5 \Rightarrow \alpha < 2.5.$
2	120	0.200	2.4	Argon	24	0.005	$\lesssim 2.5$	$\lesssim 2.5$	—	—	
3	120	0.200	2.4	Argon	24	0.005	$\lesssim 5$	$\lesssim 5$	$\lesssim 5$	$\lesssim 5$	$n > 4 \Rightarrow \alpha < 5.$
4	120	0.200	2.4	Argon	24	0.005	<5	<5	<5	<5	

Table Continues

Table D2 (Concluded) — Series—II Glow-Discharge-Cleaning Data: Grounded Polished Stainless-Steel Samples on a Lucite Holder

Sample No.	Expos. Time (min)	Current		Gas	Gas Flow Rate (cm^3/min)	Pressure (torr)	Contact Angle, α (deg)				Remarks
		Total (A)	Average (μA/cm^2)				H_2O		$I_2(CH_2)$		
							Left	Right	Left	Right	
Run 9 (6 Jan. 1975) — Test of the time until contamination after cleaned samples are exposed to laboratory air at 65° F and 40% relative humidity. The samples were cleaned at R = 38 cm.											
5	0	0	0	Air	0	760	32	30	—	—	—
6	0	0	0	Air	0	760	28	27	—	—	—
7	0	0	0	Air	0	760	—	—	40	37	—
8	0	0	0	Air	0	760	—	—	42	41	—
5	1080	0.200	2.4	Argon	28	0.005	<2.5	<2.5	<1	<1	Still inside the chamber. $n \geq 5 \Rightarrow \alpha \leq 2.5$; $n > 7 \Rightarrow \alpha < 1$.
6	1080	0.200	2.4	Argon	28	0.005	<5	<5	32	37	After 10 min out of the chamber. $n > 4 \Rightarrow \alpha < 5$.
7	1080	0.200	2.4	Argon	28	0.005	30	28	36	34	After 180 min out of the chamber.
8	1080	0.200	2.4	Argon	28	0.005	33	33	32	32	After 360 min out of the chamber.
Run 10 (7 Jan. 1975) — Samples at R = 38 cm when in the chamber											
9	0	0	0	Air	0	760	45	43	30	28	—
10	0	0	0	Air	0	760	40	40	32	28	—
9	60	0.100	1.2	Argon	30	0.005	10	10	18	18	—
10	60	0.100	1.2	Argon	30	0.005	8	9	10	10	—
11	60	0.100	1.2	Argon	30	0.005	7	6	20	18	—
12	60	0.100	1.2	Argon	30	0.005	7	6	18	15	—

Note: In Subsequent tables the gas flow rate will be expressed as millitorr-liters per minute. Since 1 atmosphere = 7.6×10^5 millitorr and 1 cm^3 = 1×10^{-3} liters, then 7.60×10^5 millitorr $\times$ 10^{-3} liters/min = 760 millitorr-liters/min. As an example, a flow of 30 cm^3/min at 1 atmosphere is 22800 millitorr-liters/min, and at a pressure of 5 millitorr this translates into 22800/5 = 4560 liters/min. From Appendix B the volume of the chamber is 2240 liters, which is (conveniently) about 2280 liters, so that a flow of 4560 liters/min represents 2 chamber volumes per minute. This approach can be applied to the preceding data as well.

Table D3a — Series-IIIA Glow-Discharge-Cleaning Data: Grounded Freshly Polished Stainless-Steel Samples on a Lucite Holder, with the Sample (Having Residual Contamination) Exposed to the Glow Discharge for 60 min at R = 18 cm in Every Run and the Pressure Being Doubled Each Time in the Sequence of Runs at a Total Current of 0.100 A (Runs 1, 3, 5, 7, 9, 10) and in the Sequence of Runs at a Total Current of 0.300 A (Runs 2, 4, 6, 8). The Gas Flow Rate was not Recorded.

Expos. Time (min)	Current		Gas	Pressure (torr	R (cm)	Contact Angle, α (deg)				Remarks
	Total (A)	Sample* (μA/cm^2)				H_2O		$I_2(CH_2)$		
						Left	Right	Left	Right	
Run 1 (10 Jan. 1975) — Sample 1										
0	0	0	Air	760	—	110	100	100	65	—
60	0.100	15.5	Argon	0.005	18	15	15	18	<2.5	n > 5 ⇒ α < 2.5
Run 2 (10 Jan. 1975) — Sample 2										
0	0	0	Air	760	—	112	105	65	63	—
60	0.300	30.2	Argon	0.005	18	<5	<5	<1.5	<1.5	n > 4 ⇒ α < 5; n > 6 ⇒ α < 1.5
Run 3 (13 Jan. 1975) — Sample 3										
0	0	0	Air	760	—	104	104	51	56	—
0	0.100	7	Argon	0.012	18	—	—	—	—	—
60	0.100	11	Argon	0.012	18	24	22	<2.5	<2.5	n > 5 ⇒ α < 2.5 Perhaps the current increases with exposure time due to reduced resistance on the surface as the sample gets cleaner.
Run 4 (13 Jan. 1975) — Sample 4										
0	0	0	Air	760	—	108	108	64	66	—
0	0.300	18.6	Argon	0.012	18	—	—	—	—	—
60	0.300	22.5	Argon	0.012	18	30	32	<2.5	<2.5	n > 5 ⇒ α < 2.5
Run 5 (13 Jan. 1975) — Sample 5										
0	0	0	Air	760	—	108	107	63	62	—
0	0.100	9.5	Argon	0.025	18	—	—	—	—	—
60	0.100	10.1	Argon	0.025	18	8	8	<5	<5	—

*Direct measurement on the sample with a microammeter.

Table D3a (Concluded) — Series-IIIA Glow-Discharge-Cleaning Data: Grounded Freshly Polished Stainless-Steel Samples on a Lucite Holder, with the Sample (Having Residual Contamination) Exposed to the Glow Discharge for 60 min at R = 18 cm in Every Run and the Pressure Being Doubled Each Time in the Sequence of Runs at a Total Current of 0.100 A (Runs 1, 3, 5, 7, 9, 10) and in the Sequence of Runs at a Total Current of 0.300 A (Runs 2, 4, 6, 8). The Gas Flow Rate was not Recorded.

Expos. Time (min)	Current		Gas	Pressure (torr)	R (cm)	Contact Angle, α (deg)				Remarks
	Total (A)	Sample* ($\mu A/cm^2$)				H_2O		$I_2(CH_2)$		
						Left	Right	Left	Right	
Run 6 (14 Jan. 1975) — Sample 6										
0	0	0	Air	760	—	112	115	65	68	—
0	0.300	14.6	Argon	0.025	18	—	—	—	—	—
60	0.300	16.3	Argon	0.025	18	8	6	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$
Run 7 (14 Jan. 1975) — Sample 7										
0	0	0	Air	760	—	100	100	60	64	—
0	0.100	3.6	Argon	0.050	18	—	—	—	—	—
60	0.100	4.1	Argon	0.050	18	8	7	<5	<5	—
Run 8 (14 Jan. 1975) — Sample 8										
0	0	0	Air	760	—	97	96	68	87	—
0	0.300	8.1	Argon	0.050	18	—	—	—	—	—
60	0.300	8.7	Argon	0.050	18	<5	<5	<5	<5	$n > 4 \Rightarrow \alpha < 5$
Run 9 (14 Jan. 1975) — Sample 9										
0	0	0	Air	760	—	106	105	61	61	—
0	0.100	6.2	Argon	0.100	18	—	—	—	—	—
60	0.100	8.5	Argon	0.100	18	10	12	13	10	—
Run 10 (15 Jan. 1975) — Sample 10										
0	0	0	Air	760	—	107	107	62	61	—
0	0.100	9.0	Argon	0.200	18	—	—	—	—	—
60	0.100	9.3	Argon	0.200	18	9	10	10	11	$n \approx 3$

Table D3b — Series-IIIB Glow-Discharge-Cleaning Data: Grounded Freshly Polished Stainless-Steel Samples on a Lucite Holder. The Exposure Time was Increased Each Run, with the Total Current Being 0.300 A and R = 18 cm for all Runs. The Date was 15 Jan. 1975.

Exposure Time (min)	Current		Gas	Pressure (torr)	R (cm)	Contact Angle, α (deg)				Remarks
	Total (A)	Sample ($\mu A/cm^2$)				H_2O		$I_2(CH_2)$		
						Left	Right	Left	Right	
Run 1 — Sample 11										
0	0	0	Air	760	—	99	101	59	61	—
0	0.300	25	Argon*	0.005	18	—	—	—	—	—
10	0.300	30	Argon*	0.005	18	12	14	41	40	—
Run 2 — Sample 12										
0	0	0	Air	760	—	105	108	60	60	—
0	0.300	31	Argon*	0.005	18	—	—	—	—	—
20	0.300	39.7	Argon*	0.005	18	—	—	15	18	
Run 3 — Sample 13										
0	0	0	Air	760	—	108	107	62	61	—
0	0.300	25	Argon*	0.005	18	—	—	—	—	—
30	0.300	31	Argon*	0.005	18	≈10	≈10	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
Run 4 — Sample 14										
0	0	0	Air	760	—	105	106	60	61	—
0	0.300	25	Argon*	0.005	18	—	—	—	—	—
60	0.300	30	Argon*	0.005	18	—	—	—	—	—
960‡	0	0	Nitrogen†	780	18	<10	<10	<2.5	<2.5	$n > 3 \Rightarrow \alpha < 10$; $n > 5 \Rightarrow \alpha < 2.5$.

*The gas flow rate was not recorded.

†The gas flow rate was zero.

‡Run 4 in series IIIB can be considered in conjunction with run 13 in series IV. In run 13 in series IV the sample was cleaned and then exposed to a low-pressure argon flow without glow-discharge cleaning overnight (18 hours = 1080 minutes) and came out as contaminated as before the cleaning, whereas in run 4 above a comparable postcleaning interval in a gas at slightly above atmospheric pressure did not result in significant recontamination of the sample. This is convincing evidence that at atmospheric pressure the outgassing and diffusion rate of contaminants from surfaces is so low that a cleaned material can be used in fabrication processes without fear of recontamination from the surfaces of its environment.

Table D4 — Series-IV Glow-Discharge-Cleaning Data: Stainless Steel Samples Alternately Grounded and Ungrounded. The Date was 16 Jan. 1975.

Exposure Time (min)	Current		Gas	Gas Flow Rate (millitorr-liters/min)	Pressure (torr)	R (cm)	Contact Angle α, (deg)				Remarks
	Total (A)	Sample ($\mu A/cm^2$)					H_2O		$I_2(CH_2)$		
							Left	Right	Left	Right	
Run 1 — Sample 1, Grounded											
0	0	0	Air	—	760	—	52	52	40	40	—
0	0.300	26.7	Argon	25,850	0.005	18	—	—	—	—	—
30	0.300	28.0	Argon	25,850	0.005	18	<10	<10	<5	<5	$n > 3 \Rightarrow \alpha < 10$; $n > 4 \Rightarrow \alpha < 5$
Run 2 — Sample 2, Ungrounded											
0	0	0	Air	—	760	—	51	51	42	42	—
30	0.300	0	Argon	27,350	0.005	18	22	20	13	12	—
Run 3 — Sample 3, Grounded											
0	0	0	Air	—	760	—	47	48	41	41	—
0	0.300	21.7	Argon	25,850	0.005	28	—	—	—	—	—
30	0.300	22.5	Argon	25,850	0.005	28	13	13	<5	<5	$n > 4 \Rightarrow \alpha < 5$
Run 4 — Sample 4, Ungrounded											
0	0	0	Air	—	760	—	50	50	42	42	—
30	0.300	0	Argon	27,350	0.005	28	8	8	<5	<5	$n > 4 \Rightarrow \alpha < 5$
Run 5 — Sample 5, Grounded											
0	0	0	Air	—	760	—	45	46	49	49	—
0	0.300	9.3	Argon	27,350	0.005	38	—	—	—	—	—
30	0.300	9.9	Argon	27,350	0.005	38	11	11	<5	<5	$n > 4 \Rightarrow \alpha < 5$
Run 6 — Sample 6, Ungrounded											
0	0	0	Air	—	760	—	45	45	42	42	—
30	0.300	0	Argon	27,350	0.005	38	8	8	<5	<5	$n > 4 \Rightarrow \alpha < 5$

Table D4 (Concluded) — Series-IV Glow-Discharge-Cleaning Data: Stainless Steel Samples Alternately Grounded and Ungrounded. The Date was 16 Jan. 1975.

Exposure Time (min)	Current		Gas	Gas Flow Rate (millitorr-liters/min)	Pressure (torr)	R (cm)	Contact Angle α, (deg)				Remarks
	Total (A)	Sample (μA/cm^2)					H_2O		$I_2(CH_2)$		
							Left	Right	Left	Right	
Run 7 — Sample 7, Grounded											
0	0	0	Air	—	760	—	51	51	38	38	—
0	0.300	7.1	Argon	50,000	0.050	18	—	—	—	—	—
30	0.300	8.8	Argon	50,000	0.050	18	21	20	7	9	—
Run 8 — Sample 8, Ungrounded											
0	0	0	Air	—	760	—	52	51	39	39	—
30	0.300	0	Argon	50,000	0.050	18	10	11	<10	<10	$n > 3 \Rightarrow \alpha < 10$
Run 9 — Sample 9, Grounded											
0	0	0	Air	—	760	—	46	46	50	48	—
0	0.300	6.2	Argon	50,000	0.050	28	—	—	—	—	—
30	0.300	6.1	Argon	50,000	0.050	28	15	16	<10	<10	$n > 3 \Rightarrow \alpha < 10$
Run 10 — Sample 10, Ungrounded											
0	0	0	Air	—	760	—	65	65	50	50	—
30	0.300	0	Argon	50,000	0.050	28	10	11	9	9	—
Run 11 — Sample 11, Grounded											
0	0	0	Air	—	760	—	65	65	58	58	—
30	0.300	—†	Argon	50,000	0.050	38	15	13	<10	<10	$n > 3 \Rightarrow \alpha < 10$
Run 12 — Sample 12, Ungrounded											
0	0	0	Air	—	760	—	35	35	43	43	—
30	0.300	0	Argon	50,000	0.050	38	11	11	<5	<5	$n > 4 \Rightarrow \alpha < 5$
Run 13 — Sample 13, Grounded											
0	0	0	Air	—	760	—	63	64	44	45	—
30	0.300	0†	Argon	23,480	0.005	18	—	—	—	—	—
1080*	0	0	Argon	23,480	0.005	18	65	65	58	58	Low press. overnight

*Footnote on Table D3b.

†The microammeter had been borrowed and was returned.

Table D5 — Series-V Glow-Discharge-Cleaning Data: Aluminum Oxide (Al_2O_3) Gyroscope Bearings (Avco). Sample currents were not measured because the borrowed microammeter had been returned

Sample side	Expos-Time (min)	Total Current (A)	Gas	Gas Flow Rate (millitorr-liters/min)	Pressure (torr)	R (cm)	Contact Angle, α (deg)				Remarks
							H_2O		$I_2(CH_2)$		
							Left	Right	Left	Right	
Run 1 — 30 min at 0.010 torr											
1-1	0	0	Air	0	760	—	69	70	49	48	—
1-1	30	0.100	Argon	28,900	0.010	18	14	15	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
2-1	0	0	Air	0	760	—	63	61	41	43	—
2-1	30	0.200	Argon	28,900	0.010	18	16	16	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
Run 2 — 30 min at 0.010 torr											
1-2	0	0	Air	0	760	—	75	74	52	52	—
1-2	30	0.300	Argon	28,900	0.010	18	11	12	10	9	—
2-2	0	0	Air	0	760	—	—	—	—	—	—
2-2	30	0.400	Argon	28,900	0.010	18	8	7	<10	<10	$n > 3 \Rightarrow \alpha < 10$
Run 3 — 60 min at 0.005 torr											
1-1	0	0	Air	0	760	—	40	40	35	33	—
1-1	60	0.100	Argon	27,000	0.005	18	14	14	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
1-2	0	0	Air	0	760	—	56	56	50	50	—
1-2	60	0.200	Argon	27,000	0.005	18	14	14	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
Run 4 — 60 min at 0.005 torr											
2-1	0	0	Air	0	760	—	45	45	38	37	—
2-1	60	0.300	Argon	23,600	0.005	18	9	7	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
2-2	0	0	Air	0	760	—	49	50	41	42	—
2-2	60	0.400	Argon	25,100	0.005	18	13	14	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
Run 5 — 15 hours at 0.012 torr											
1-1	0	0	Air	0	760	—	55	55	47	46	—
1-1	900	0.100	Argon	?	0.012	18	<2.5	<2.5	<1	<1	$n > 5 \Rightarrow \alpha < 2.5$; $n > 7 \Rightarrow \alpha < 1$.
2-1	0	0	Air	0	760	—	50	51	47	46	—
2-1	900	0.100	Argon	?	0.012	18	<2.5	<2.5	<1	<1	$n > 5$; $n > 7$.

Table D6a — Series-VIA Glow-Discharge-Cleaning Data: Synthetic Rubies and Sapphires (Al_2O_3)

Sample No.	Expos. Time (min)	Current		Gas	Gas Flow (mtorr-1/min)	Pressure (torr)	R (cm)	Contact Angle, α (deg)				Remarks
		Total (A)	Average (μA/cm²)					H_2O		$I_2(CH_2)$		
								Left	Right	Left	Right	
Run 1 — At 350 V												
Ruby	0	0	0	Air	0	760	—	68	72	30	28	—
1	60	0.200	2.4	Argon	16,000	0.005	18	—	—	<1	<1	$n > 7 \Rightarrow \alpha < 1$.
Sapphire	0	0	0	Air	0	760	—	48	48	32	32	—
1	60	0.200	2.4	Argon	16,000	0.005	18	<5	<5	—	—	$n > 4 \Rightarrow \alpha < 5$.
Run 2 — At 405 V												
Ruby	0	0	0	Air	0	760	—	56	58	31	31	—
2	60	0.200	2.4	Argon	22,000	0.0033	18	<10	<10	—	—	$n > 3 \Rightarrow \alpha < 10$.
Sapphire	0	0	0	Air	0	760	—	62	62	32	32	—
2	60	0.200	2.4	Argon	22,000	0.0033	18	4; <5	<5	<10	<10	$n > 4; n > 3$.
Run 3 — At 450 V												
Ruby	0	0	0	Air	0	760	—	51	51	30	31	—
3	60	0.200	2.4	Argon	11,500	0.002	18	—	—	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
Sapphire	0	0	0	Air	0	760	—	53	55	40	37	—
3	60	0.200	2.4	Argon	11,500	0.002	18	<5	<5	<5	<5	$n > 4 \Rightarrow \alpha < 5$.

Table D6b — Series-VIB Glow-Discharge-Cleaning Data: Al_2O_3 Avco Bearings

Sample No.	Expos. Time (min)	Current		Gas	Gas Flow (mtorr-1/min)	Pressure (torr)	R (cm)	Contact Angle, α (deg)				Remarks
		Total (A)	Average (μA/cm²)					H_2O		$I_2(CH_2)$		
								Left	Right	Left	Right	
Run 4 — At 405 V												
1-1	0	0	0	Air	0	760	—	45	48	28	27	—
1-1	60	0.200	2.4	Argon	20,500	0.0033	18	<5	<5	5; <5	3; <5	$n > 4 \Rightarrow \alpha < 5$.
2-1	0	0	0	Air	0	760	—	40	41	34	30	—
2-1	60	0.200	2.4	Argon	20,500	0.0033	18	6; <10	7; <10	<5	<5	$n > 3; n > 4$.
Run 5 — At 450 V												
1-2	0	0	0	Air	0	760	—	70	70	—	—	—
1-2	60	0.200	2.4	Argon	11,400	0.002	18	<5	<5	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
1-2	2	0	0	Rm air	0	—	—	—	—	25	25	—
2-2	0	0	0	Air	0	760	—	72	68	—	—	—
2-2	60	0.200	2.4	Argon	11,400	0.002	18	<2.5	<2.5	<5	<5	$n > 5; n > 4$.
2-2	3	0	0	Rm air	0	—	—	5	4	—	—	—

Table 7 — Series-VII (Run 1) Glow-Discharge Cleaning Data: Samples Precontaminated with Dow Corning Pump Oil No. 704 (Silicone Oil) Overnight and Then Washed, Rinsed, and Air Dried.

Sample		Expos. Time* (min)	Current		Gas	Gas Flow (mtorr-l/min)	Pressure (torr)	R (cm)	Contact Angle, α (deg)				Remarks
Type	No. and Side		Total (A)	Average ($\mu A/cm^2$)					H_2O		$I_2(CH_2)$		
									Left	Right	Left	Right	
Al_2O_3 bearing	1-1	0	0	0	Air	0	760	—	77	72	37	37	—
		120	0.200	2.4	Argon	22,800	0.002	18	15	13	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
		240	0.200	2.4	Argon	22,800	0.002	18	<5	<5	<2.5	<2.5	$n > 4; n > 5$.
		340	0.200	2.4	Argon	22,800	0.002	18	<5	<5	<2.5	<2.5	$n > 4; n > 5$.
	2-1	0	0	0	Air	0	760	—	70	72	41	42	—
		120	0.200	2.4	Argon	22,800	0.002	18	15	15	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
		240	0.200	2.4	Argon	22,800	0.002	18	<5	<5	<2.5	<2.5	$n > 4; n > 5$.
		340	0.200	2.4	Argon	22,800	0.002	18	<2.5	<2.5	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
Ruby	3	0	0	0	Air	0	760	—	62	63	33	33	—
		120	0.200	2.4	Argon	22,800	0.002	18	—	—	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
		240	0.200	2.4	Argon	22,800	0.002	18	—	—	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
		340	0.200	2.4	Argon	22,800	0.002	18	<5	<5	—	—	$n > 4 \Rightarrow \alpha < 5$.
Sapphire	4	0	0	0	Air	0	760	—	68	73	43	43	—
		120	0.200	2.4	Argon	22,800	0.002	18	14	<5	<5	<5	$n > 4 \Rightarrow \alpha < 5$.
		240	0.200	2.4	Argon	22,800	0.002	18	<2.5	<2.5	—	—	$n > 5 \Rightarrow \alpha < 2.5$.
		340	0.200	2.4	Argon	22,800	0.002	18	—	—	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
Stainless steel	5	0	0	0	Air	0	760	—	63	63	43	43	—
		120	0.200	2.4	Argon	22,800	0.002	18	13	18	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
		240	0.200	2.4	Argon	22,800	0.002	18	6	5	<1.5	<1.5	$n > 6 \Rightarrow \alpha < 1.5$.
		340	0.200	2.4	Argon	22,800	0.002	18	<5	<5	<1.5	<1.5	$n > 4; n > 6$.
Stainless steel	6	0	0	0	Air	0	760	—	55	59	42	43	—
		120	0.200	2.4	Argon	22,800	0.002	18	20	18	<2.5	<2.5	$n > 5 \Rightarrow \alpha < 2.5$.
		240	0.200	2.4	Argon	22,800	0.002	18	9	7	<1.5	<1.5	$n > 6 \Rightarrow \alpha < 1.5$.
		340	0.200	2.4	Argon	22,800	0.002	18	<5	<5	<1.5	<1.5	$n > 4; n > 6$.

*The vacuum system was backfilled with nitrogen at the end of each time interval for contact-angle measurements on all samples before restarting. Therefore the time is accumulative, and the samples were recontaminated with $I_2(CH_2)$ and H_2O by the contact-angle measurements.

Reprint of NRL Memorandum Report 3201

A Method to Estimate the Contact Angle of a Drop Spread Upon a Flat Surface when it is Otherwise too Flat to Measure

INTRODUCTION

In the course of measuring the amount of contamination present on a clean surface after cleaning, a relationship between the contact angle of a small drop on the surface and the contamination is used according to established criteria (see Refs. 1 - 4).

The contact angle is measured with the use of a small microscope and its appropriate lighting system called a Goniometer. The angle measurements become increasingly vague and difficult as the drop spreads and the contact angle becomes less than 5°. This has not caused a great deal of concern, since in the past most contact angles were greater than 15°. However, during an experiment using an improved method of plasma cleaning of surfaces it was found that the drop spread so thin on the surface that its profile could not always be observed. Such is often the case when the contact angle is 5° or less. This memorandum discusses a means of estimating the contact angle from 10° to 0.5° with a certainty which is dependent on the accuracy of the knowledge of the volume of the original drop, and its diameter when spread out over the surface of the clean specimen.

The experiment data to test the following theory, was accumulated by measuring drops on optically flat specimens made of stainless steel, sapphire, ruby and an aluminum oxide bearing. The angles were measured from photographs so that the height to diameter ratio and contact angle measurements could be fixed in time, since the drop size changed rather rapidly as a function of time, (evaporation rate, and recontamination rate). The data is plotted in Fig. 3 and tabulated in Table 1.

Note: Manuscript submitted December 24, 1975.

For the purposes of this analysis a small drop is defined as a drop size where the maximum hydrostatic force within a drop resting on a clean surface is less than the force due to surface tension acting the drop. Experimental evidence included in the subsequent data confirms the definition within the limits of the observations.

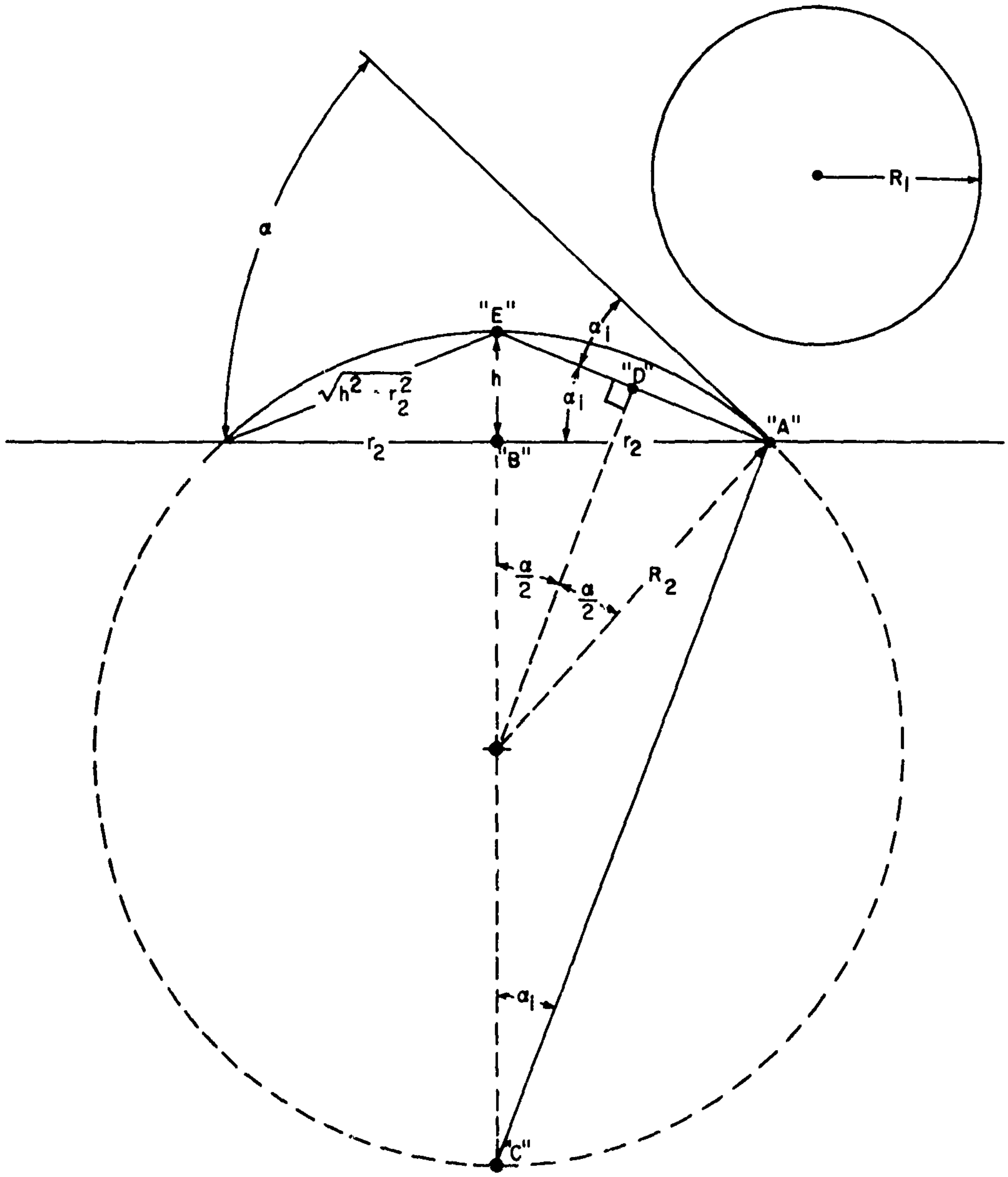


Fig. 1 - The geometrical relationship of the contact angle of a small drop on a level, flat surface, to a spherical drop of equal volume

Section 1

The spreading ratio

If it is assumed that a small drop spreading evenly on a flat surface forms a spherical segment, then the relationship of the diameter of the initial drop before contact can be related to the diameter of the spherical segment by the fact they have equal volumes. Thus by simple geometry

$$\text{Volume of Sphere} = \frac{3}{4}\pi R_1^3 \quad . \tag{1}$$

$$\text{Volume of spherical segment} \equiv \frac{1}{3}\pi h^2(3\ R_2 + h) \quad , \tag{2}$$

where h = height of segment (Fig. 1)

R_2 = radius of curvature of the segment

R_1 = radius of the initial drop, and

define $nR_1 = r_2$ = radius of the segment base.

Then combining Eqs. (1) and (2), r_2 is related to R_2 by 3.

$$\frac{4}{n^3}\ r_2^3 = h^2(3\ R_2 - h). \quad \text{"n" is the spreading ratio.} \tag{3}$$

From the geometry it can be seen that

$$\operatorname{Sin} \alpha/2 \equiv \frac{1}{2}\sqrt{h^2 + r_2^2/R_2} \equiv \sqrt{\frac{h^2 + r_2^2}{2\ R_2}} \equiv \operatorname{Sin} \alpha_i \tag{3a}$$

because of similar triangles, and because

α = the contact angle = 2 α_i,

then

$$\operatorname{Tan} \alpha_i = h/r_2 = \frac{r_2}{2\ R_2 - h} \quad . \tag{3b}$$

Thus

$$\alpha = 2\ \tan^{-1} h/r_2 \quad \text{and} \tag{3c}$$

$$r_2^2 = h(2R_2 - h) \quad . \tag{4}$$

Combine Eq's (3) and (4) to eliminate R_2, then simplify to

$$\frac{4r^3}{n^3} = \frac{h}{2}(3r_2^2 + h^2),$$

thus

$$\frac{1}{n^3} = \frac{1}{8}\left[\frac{h}{r_2}\left(3 + \frac{h^2}{r_2^2}\right)\right] \quad . \tag{5}$$

Solve for n ,

$$n = 2\left[\frac{h}{r_2}\left(3 + \frac{h^2}{r_2^2}\right)\right]^{-\frac{1}{3}} = 2\cot\frac{\alpha}{2}\left[1 + \cot^2\frac{\alpha}{2}\right]^{-\frac{1}{3}} \quad . \tag{6}$$

Equation (5) is used to calculate the curve (nomograph) of contact angle vs n (Fig. 2).

If a small drop spreading evenly on a flat surface forms a spherical segment of a larger sphere, then $\alpha/2 = \tan^{-1} h/r_2$. Therefore the measurement of the α_is, h_i's and r_{2i}'s for a series of different drops should, within the precision of the measurements, correspond to the geometric relationship.

A series of photographs were taken of drops on surfaces with different degrees of contamination.

The results of the measurements are points α vs h/r_2 from Eq. (3c).

The fact that most of the points are below the line may indicate a systematic error in the measurements, or it may indicate that the shape of the assumed spherical segment becomes a little flat as the radius of curvature increases. In either case the observed angles are slightly less than they would be if calculated from the observed h/r_2.

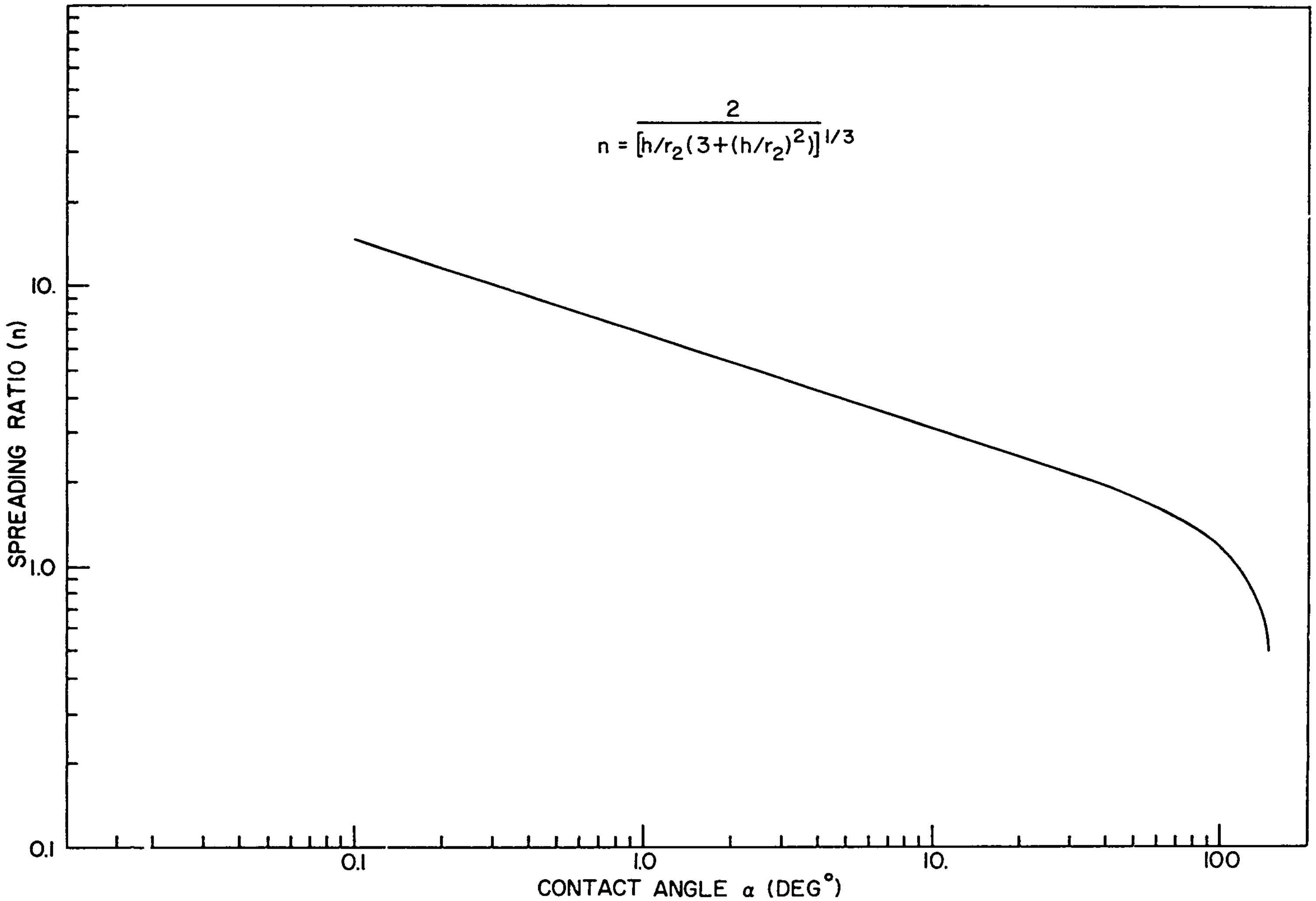


Fig. 2 - Contact angle (α) vs spreading ratio (n) for spherical segments

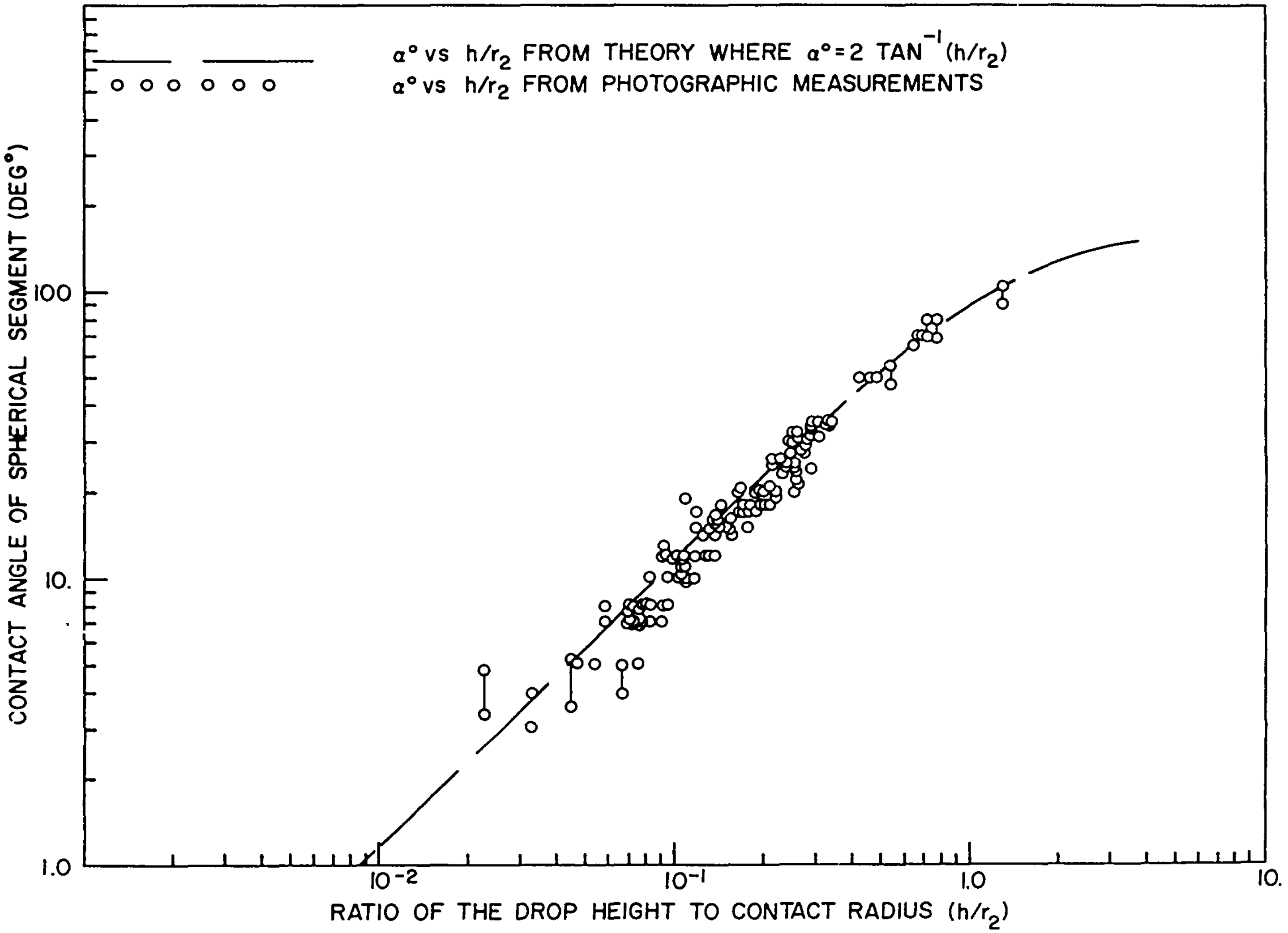


Fig. 3 - Summary of measured contact angle vs measured h/r_2 compared to theory where $\alpha = 2 \tan^{-1} (h/r_2)$

Table 1

Contact Angle vs Spreading Ratio
Measurements from Photographs of Drop Profiles on Surfaces

Photographic			Sample		Exposure Time		Measured Parameters				Calculated Parameters		
							Angle(α)						
Roll	Frame	Drop Type	Type	Number	To Air Min	To Film Sec	Left	Right	Height h	Dia. d_2	Radius r_2	Ratio h/r_2	α' deg^o
1	0	H_2O	St.Steel	1	1	1/30	$\alpha < 5^o$	$\alpha < 5^o$	0.4	35.4	17.7	0.0226	2.59
"	1	"	"	"	2	"	5	-	-	-	-	-	-
"	2	"	"	"	3	"	8	8	-	-	-	-	-
"	3	"	"	"	5	"	5	5	-	-	-	-	-
"	4	"	"	"	6	"	-	-	-	-	-	-	-
"	5	"	"	2	2	"	8	-	-	-	-	-	-
"	6	"	"	"	3	"	-	-	-	-	-	-	-
"	7	"	"	"	4	"	-	7	1.3	34	17	.07647	8.75
"	8	"	"	"	8	"	-	12	1.6	34	17	.09411	10.75
"	9	"	"	"	9	"	3	4	0.6	36	18	.03333	3.82
"	10	"	"	"	11	"	20	-	3.1	38	19	.16316	18.53
"	11	"	"	"	13	"	7	8	1.8	46	23	.07826	8.95
"	12	"	"	3	15	"	7	8	1.2	34	17	.07059	8.08
"	13	"	"	"	15	"	5	-	0.9	38	19	.04737	5.42
"	14	"	"	"	17	"	8	8	1.3	34	17	.07647	8.75
"	15	"	"	"	18	"	18	-	2.7	38	19	.142105	16.18
"	16	"	"	"	19	"	8	10	1.6	33	16.5	.09697	11.08
"	17	"	"	"	20	"	15	16	2.1	31	15.5	.13548	15.43
"	18	"	"	"	23	"	7	8	1.2	32	16	.075	8.58
"	19	"	"	"	25	"	6	7	1.3	36	18	.07222	8.26
"	20	"	"	"	27	"	20	17	2.4	29	14.5	.16552	18.80

Table 1 (cont.)

Contact Angle vs Spreading Ratio
Measurements from Photographs of Drop Profiles on Surfaces

Photographic			Sample		Exposure Time		Measured Parameters				Calculated Parameters		
Roll	Frame	Drop Type	Type	Number	To Air Min	To Film Sec	Angle(α) Left	Angle(α) Right	Height h	Dia. d_2	Radius r_2	Ratio h/r_2	α' deg^o
2	0	H_2O	St.Steel	4	31	1/30	-	-					
"	1	"	"	"	34	"	-	5	-	-	-	-	-
"	2	"	"	"	35	"	5	-	1.2	44	22	.05455	6.24
"	3	"	"	"	35	"	5	7	1.1	28.7	14.35	.07666	8.77
"	4	"	"	"	36	"	14	16	2.0	28.9	14.45	.1380	15.76
"	5	"	"	"	37	"	20	18	2.8	28.4	14.2	.19718	22.31
"	6	"	"	"	39	"	15	-	2.4	32.0	16.0	.15000	17.06
"	7	"	"	"	40	"	7	8	1.3	32.1	16.05	.08100	9.26
"	8	"	"	1	46	"	20	17	3.0	31.7	15.85	.18927	21.44
"	9	"	"	"	47	"	7	8	2.3	60	30.0	.076666	8.77
"	10	"	"	"	48	"	10	12	1.5	29.0	14.5	.10345	11.81
"	11	"	"	"	49		out of focus		-	-	-	-	-
"	12	"	"	"	49	"	18	-	3.1	34.0	17.0	.18235	20.67
"	13	"	"	2	45	"	15	-	2.6	34.0	17.0	.15294	17.39
"	14	"	"	"	46	"	15	15	2.5	28.0	14.0	.17857	20.25
"	15	"	"	"	47	"	-	17	3.5	39.0	19.5	.17949	20.35
"	16	"	"	"	48	"	25	27	2.1	17.1	8.55	.24561	27.60
"	17	$I_2(CH_2)$	"	3	49	"	out of focus		-	-	-	-	-
"	18	"	"	"	49	"	27	30	4.0	29.1	14.55	.274914	30.74
"	19	"	"	"	50	"	out of focus		-	-	-	-	-
"	20	"	"	"	52	"	out of focus		-	-	-	-	-

Table 1 (cont.)

Contact Angle vs Spreading Ratio
Measurements from Photographs of Drop Profiles on Surfaces

Photographic			Sample		Exposure Time		Measured Parameters				Calculated Parameters		
Roll	Frame	Drop Type	Type	Number	To Air Min	To Film Sec	Angle(α) Left	Angle(α) Right	Height h	Dia. d_2	Radius r_2	Ratio h/r_2	α' deg^o
3	0	$I_2(CH_2)$	St.Steel	5	51	1/30	Poor	Focus					
"	1	"	"	"	51	"	Poor	Focus					
"	2	H_2O	"	6	53	"	Poor	Focus					
"	3	"	"	"	54	"	95 - 100	95 - 100	9.6	17	8.5	1.294	96.95
"	4	"	"	"	56	"	65 - 67	65 - 67	8.1	24.3	12.15	.66666	67.38
"	5	"	"	"	58	"	65	67	8.1	24.8	12.4	.65322	66.3
"	6	"	"	7	No	"	71	75	8.1	20.9	10.45	.77512	75.0
"	7	-	-	-	Time	"	Missing	-	-	-	-	-	-
"	8	$I_2(CH_2)$	"	"	Record	"	18	20	3.2	32.0	16.0	.200	22.6
"	9	"	"	"	"	"	23	25	3.1	26.7	13.35	.2322	26.1
"	10	"	"	"	"	"	25	25	3.1	26.5	13.25	.2339	26.3
"	11	"	"	"	"	"	28	28	3.7	26.7	13.35	.2771	30.2
"	12	"	"	"	"	"	29	30	3.9	32.0	16.0	.24375	27.4
"	13	H_2O	"	8	"	"		Off	Balance				
"	14	"	"	"	"	"		"	"				
"	15	"	"	"	"	"		"	"				
"	16	"	Ruby	9	"	"	70 - 75	70 - 75	7.6	21.3	10.65	.7136	71.0
"	17	$I_2(CH_2)$	Ruby	"				Poor	Focus				
"	18	H_2O	Sapphire	10	"	"	49 - 51	52 - 53	6.8	25.0	12.50	.544	57.1
"	19	$I_2(CH_2)$	"	"	"	"		Poor	Focus				
"	20	"	"	"	"	"	50	50	4.7	22.2	11.10	.42342	45.90

Table 1 (cont.)

Contact Angle vs Spreading Ratio
Measurements from Photographs of Drop Profiles on Surfaces

Photographic			Sample		Exposure Time		Measured Parameters				Calculated Parameters		
							Angle(α)						
Roll	Frame	Drop Type	Type	Number	To Air Min	To Film Sec	Left	Right	Height h	Dia. d_2	Radius r_2	Ratio h/r_2	α' deg°
4	1	H_2O	St.Steel	1	Time	1/30	≈ 70°		5.8	8.0	4.0	.72500	71.88
"	2	"	"	2	Record	"	≈ 70°		10.3	30.8	15.4	.66883	67.55
"	3	"	"	3	"	"	≈ 70°		10.7	30.8	15.4	.694805	69.58
"	4	"	"	4	"	"	30		2.4	18.6	9.3	.25806	28.94
"	5	"	"	5	"	"	≈ 50		2.25	9.8	4.9	.45918	49.33
5	2	"	"	5	"	"	-	12	2.2	32	16	.1375	15.66
"	3	"	"	6	"	"	-	12	2.1	32	16	.13125	14.95
"	4	"	"	7	"	"	20	18	2.0	18.7	9.35	.21390	24.15
"	5	"	"	8	"	"	25	25	2.6	22.0	11.0	.23636	26.60
"	6	"	"	9	"	"	-	13	1.6	32	16.0	.10000	11.42
"	7	"	"	10	"	"	-	13	2.0	32	16.0	.12500	14.25
"	8	"	"	11	"	"	15	15	1.1	15.8	7.9	.13924	15.85
"	9	"	"	12	"	"	17	18	1.8	21.3	10.65	.16901	19.19
"	10	"	"	13	"	"	16	15	2.1	30.5	15.25	.137705	15.68
"	11	"	"	14	"	"	10 - 12	12	1.5	25.6	12.8	.117187	13.37
"	12	"	"	15	"	"	10	11	1.4	25.6	12.8	.109375	12.48
"	13	"	"	16	"	"	10	10	1.4	"	"	"	12.48
"	14	"	"	1	"	"	10	10	1.4	"	"	"	12.48
"	15	"	"	2	"	"	8	7	1.4	30.4	15.2	.092105	10.52
"	16	"	"	3	"	"	-	-	2.0	-	-		-
"	17	"	"	4	"	"	10 - 12	-	2.2	41.0	20.5	.107317	12.25

Table 1 (cont.)

Contact Angle vs Spreading Ratio
Measurements from Photographs of Drop Profiles on Surfaces

Photographic		Drop Type	Sample		Exposure Time		Measured Parameters				Calculated Parameters		
							Angle(α)						
Roll	Frame		Type	Number	To Air Min	To Film Sec	Left	Right	Height h	Dia. d_2	Radius r_2	Ratio h/r_2	α' deg^o
5	18	H_2O	St.Steel	5		1/30	2 - 3						
"	19	"	"	5		"	-	-	0.7	≈ 66.8	33.4	.002096	2.40
"	20	"	"	5				2 - 3					
"	21	"	"	6		"	7 - 8						
"	22	"	"	6		"	-	-	1.4	33.1	16.55	.08459	9.67
"	23	"	"	6		"		7 - 8					
"	24	"	"	7		"	7	8	1.1	26.3	13.15	.08365	9.56
"	25	"	"	8		"	10						
"	26	"	"	8		"			1.7	≈34.0	17	.10000	11.42
"	27	"	"	8		"		9					
"	28	"	"	9		"	7	8	0.6	20.5	10.25	.05854	6.70
"	29	"	"	10		"	10	10	1.0	24.0	12.0	.08333	9.53
"	30	"	"	11		"	19 - 12	11	1.3	24.0	12.0	.10833	12.36
"	31	"	"	12		"	15	15	1.6	24.1	12.05	.13278	15.13
"	32	"	"	13		"	7	7	1.0	27.6	13.8	.07246	8.29
"	33	"	"	14		"	25	26	2.7	25.1	12.55	.21514	24.28
"	34	"	"	15		"	35	35	3.5	24.2	12.10	.28926	32.26
"	35	"	"	16		"	13	12	0.9	19.7	9.85	.09137	10.44
"	36	"	"	1		"	50	50	5.7	23.6	11.80	.48305	51.56

Table 1 (cont.)

Contact Angle vs Spreading Ratio
Measurements from Photographs of Drop Profiles on Surfaces

Photographic			Sample		Exposure Time		Measured Parameters				Calculated Parameters		
Roll	Frame	Drop Type	Type	Number	To Air Min	To Film Sec	Angle(α)		Height h	Dia. d_2	Radius r_2	Ratio h/r_2	θ' deg°
							Left	Right					
6	1	H_2O	St.Steel	2		1/30	$\alpha < 5^\circ$	-	0.8	23.4	11.7	.05838	7.82
"	2	"	"	3		"	$\alpha < 5^\circ$						
"	3	"	"	3		"		$\alpha < 5^\circ$	0.5	25.0	12.5	.04000	4.58
"	4	"	"	4		"	3						
"	5	"	"	4		"			0.7	36	18.0	.038889	4.45
"	6	"	"	4		"		3 - 4					
"	7	"	"	5		"	12	12	1.5	23.3	11.65	.12875	14.67
"	8	"	"	6		"	14	14	2.0	31.8	15.9	.12579	14.34
"	9	"	"	7		"	17	15	1.9	31.8	15.9	.11950	13.63
"	10	"	"	8		"	15 - 17						
"	11	"	"	8		"			2.4	34.5	17.25	.13913	15.84
"	12	"	"	8		"		15 - 16					
"	13	"	"	9		"	14 - 16						
"	14	"	"	9					3.0	34.2	17.1	.17544	19.9
"	15	"	"	9		"		15 - 17					
"	16	"	"	10		"	5 - 7						
	17	"	"	10		"	-	-	1.0	35.0	17.5	.05914	6.54

Table 1 (cont.)

Contact Angle vs Spreading Ratio
Measurements from Photographs of Drop Profiles on Surfaces

Photographic		Drop Type	Sample		Exposure Time		Measured Parameters				Calculated Parameters		
Roll	Frame		Type	Number	To Air Min	To Film Sec	Angle(α) Left	Angle(α) Right	Height h	Dia. d_2	Radius r_2	Ratio h/r_2	α' deg^o
6	18	H_2O	St.Steel	10		1/30		4 - 5	-				
"	19	"	"	11		"	34	34	4.2	25.0	12.5	.33600	37.14
"	20	"	"	12		"	35	37	5.0	29.4	14.7	.34014	37.57
"	21	"	"	13		"	35	34	1.9	12.7	6.35	.29921	33.32
"	22	"	"	14		"	31	32	3.0	23.9	11.95	.25105	28.19
"	23	"	"	15		"	31	32	3.1	23.1	11.55	.26840	30.05
"	24	"	"	16		"	26	26	3.4	28.8	14.4	.23611	26.57
"	25	"	"	1		"	34	34	3.7	22.3	11.15	.33184	36.72
"	26	"	"	2		"	29	30	3.5	25.1	12.55	.27888	31.17
"	27	"	"	3		"	19	20	2.9	25.6	12.8	.22656	25.53
"	28	"	"	4		"	20	22	4.0	31.3	15.65	.25559	28.67
"	29	"	"	5		"	25	24	4.0	31.3	15.65	.25559	28.67
"	30	"	"	6		"	23	22	4.0	31.3	15.65	.25559	28.67
"	31	"	"	7		"	33	32	3.3	23.0	11.5	.28696	32.02
"	32	"	"	8		"	31	31	4.4	28.1	14.05	.31317	34.78
"	33	"	"	9		"	20	20	2.9	28.8	14.4	.20139	22.77
"	34	"	"	10		"	24	24	4.2	28.8	14.4	.29167	32.5
"	35	"	"	11		"	35	35	4.5	29.0	14.5	.31034	34.48
"	36	"	"	12		"	-	12	2.0	39.0	19.5	.10256	11.71

For the purpose of estimating contact angles, the curve in Fig. 3 was assumed to be essentially correct for contact angles down to 1.0 degree where $6 < n < 7$ and the corresponding value of $h/r_2 = 8.727 \times 10^{-3}$.

All estimations of "n" were deliberately conservative. For "example" when n appeared to be at least 9 but possibly 8, $n > 7$ was the ratio chosen on the side of caution, and implies that $\alpha < 1^{\circ}$. Hence the recorded notation; $n > 7 \rightarrow \alpha\ 1^{\circ}$. Allowance for over estimating the spreading ratio is about 25%. Therefore it is assumed that all the contact angle estimates are at the larger limit, but the actual contact angles are often significantly smaller. An accurate measurement of the spreading ratio may be available in the future if more sophisticated optical instrumentations becomes available.

D_1 was determined by using a fine hypodermic needle as a drop source and counting the number of apparently uniform size drops on an optically flat surface. A 1,000 μ liter gas tight #1001 syringe was used with a #25 size hypodermic needle the results are shown in Table 2. A slightly smaller drop was obtained when using the same size needle coated with a fluoro-carbon compound (5) to reduce its surface energy but the difference in the volume was reduced only about 1/3 and the resulting reduction in diameter was only about 15%. For the purposes of this experiment, the reduction of the drop diameter was too small to be significant.

Section 2

Drop size criteria

This section represents an attempt to establish a reasonable criteria for choosing a drop size which yields a spherical segment, as suggested by the definition accompanying Fig. 1. A small drop is defined as a drop size where the maximum hydrostatic force due to gravity is less than the force due to surface tension acting on the drop.

The pressure due to gravity is

$$P_g = (h - h_i)g\rho \quad , \qquad (6)$$

where

P_g = hydrostatic pressure due to gravity

h = height of the drop

h_i = height of pressure point above the base

ρ = density of the liquid in the drop

g = acceleration of gravity

From Eq. (3a) $\alpha/2 = \alpha_i$, thus $\tan \alpha/2 = h/r_2$ and $h = r_2 \tan \alpha/2$. Therefore when $h_i = 0$

$$P_g = (r_2 \tan \alpha/2)\, g\rho \text{ is a maximum pressure.} \tag{7}$$

$$P_T = \frac{2\,\sigma}{R_2} = \text{pressure within the spherical segment due to surface tension. From Eq. (4)} \tag{8}$$

$r_2^2 = h(2\,R_2 - h)$, therefore

$$R_2 = \frac{1}{2\,h}\,(r_2^2 + h^2) \equiv \frac{r_2}{2 \sin \alpha/2 \cos \alpha/2} .$$

Thus

$$P_T = \frac{4\,\sigma\,(\sin \alpha/2 \cos \alpha/2)}{r_2} . \tag{9}$$

Therefore, since the arbitrary criteria for a small drop requires that $P_g < P_T$ then $P_T/P_g > 1$. However,

$$P_T/P_g = \frac{4\,\sigma\,(\sin \alpha/2 \cos \alpha/2)}{r_2(r_2 \tan \alpha/2)g\rho} > 1 ,$$

which is identical to

$$\frac{4\,\sigma \cos^2 \alpha/2}{r_2^2\, g\rho} > 1, \quad \text{or} \quad \frac{4\,\sigma \cos^2 \alpha/2}{(nR_1)^2\, g\rho} > 1 ,$$

where R_1 is the radius of the small drop and "n" is the spreading ratio.

Assume a range of values $0.3^\circ < \alpha < 20^\circ$
according to Eq. (4) $10 > n > 2.5$
and in the same order, $0.999996 \geq \cos \alpha/2 \geq 0.9848$,

then

$$n < \sqrt{\frac{4\ \sigma \cos^2 \alpha/2}{R_1^2\ g\rho}} \equiv \frac{2 \cos \alpha/2}{R_1} \sqrt{\sigma/g\rho} .$$

Consider a drop of water, $\sigma \cong 72$ dynes/cm, $\rho \cong 1$ gm/cm^3, $g = 980$ cm/sec^2.

$$n < \frac{0.5338 \text{ cms}}{R_1 \text{ cms}} ,$$

the average drop diameter of water in Table 2 was 0.2616 cms

$$R_1 = \frac{.2616}{2} = .1308 \text{ cms},$$

therefore $n < 4.08$. This implies that as long as the spreading ratio is less than 4 the criteria for drop size is met. The fact that the shape approximates a spherical segment, does not mean that I pretend to imply that this criteria proves that the drop will have a spherical shape. It is only a means to keep the drop within a reproducible size. Then, within this size limitation the curve illustrated in Fig. 3 of h/r_2 to α will produce an experimental verification of the method of determining the contact angle within the observed range.

Table 2

Determination of Drop Diameters
"A" Using a Clean #25 Hypodermic Needle with a Squared off Tip

	Type of Liquid	Total Volume mm^3	Number of Drops	Average Drop Volume mm^3	Average Drop Diam. mm	Max. "n"
1.)	H_2O	1000 ± 5	107	9.3458		
2.)	H_2O	1000 ± 5	104	9.6154		
3.)	H_2O	1000 ± 5	109	9.1734		
				9.3750	2.616	4.08
4.)	2 - Propanol	1000 ± 5	234	4.2735		
5.)	2 - Propanol	1000 ± 5	242	4.1322		
6.)	2 - Propanol	1000 ± 5	237	4.2194		
				4.2075	2.005	
7.)	$I_2(CH_2)$	500 ± 5	262	1.9084	1.539	3.11
	"B" using a clean #25 needle similar "A" but coated with [Poly-C_{17} F_{15} CH_2OOCC (CH_3) = CH_2]					
8.)	H_2O	1000 ± 5	171	5.8479	2.235	4.78

To use a check for internal consistency, the tensile strength of the drop should be proportional to its surface tension, thus to the mass of the largest drop suspended from the needles point. At 20°C we have ωT of $H_2O = 4/3\,\pi(R_1^3)(\rho_1) = K_1\gamma_1$. Similarly ωT of $I_2(CH_2) = K_2\gamma_2$

$$\therefore \frac{(K_1\gamma_2)}{K_2\gamma_2} = \frac{\omega T(H_2O)}{\omega T(I_2CH_2)} \quad \text{and} \quad \gamma_2 = \frac{R_2^3\rho_2\gamma_1}{R_1^3\rho_1} \quad \gamma_1 = 78 \text{ dynes/cm}, \ \rho_1 = 1, \ \rho_2 = 3.3.$$

Substituting $R_1 = 2.616/2$ and $R_2 = 1.539/2$. $\gamma_2 \cong 52.4$ dynes/cm which compares well with the accepted value of 51.8 dynes/cms.