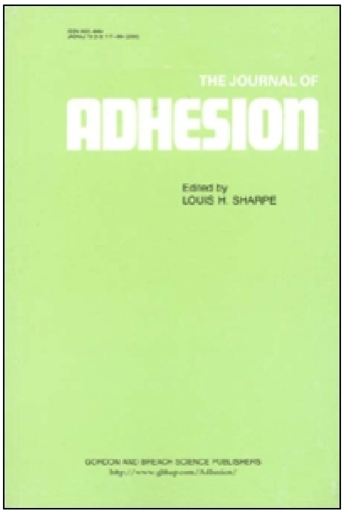

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Surface Treatment and its Influence on Contact Angles of Water Drops Residing on Teflon and Copper

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Note

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INTRODUCTION

The variation of contact angle of liquid sessile drops on solids has been attributed to roughness (Wenzel[1]), the static charge effect (Holly,[2] Ponter and Yekta-Fard[3]) and contamination at the solid surface or in the liquid and gaseous phases.

The scope of this paper is limited to the effects of contamination and surface preparation on the contact angle of water on copper and Teflon (PTFE) at ambient temperature and in water-saturated atmospheres of argon or nitrogen.

The wetting of a copper surface is not only influenced by contamination but additionally by the chemical reaction with water and oxygen. Horsthemke and Schröder[4] have measured contact angles of water on copper surfaces which had been exposed to distilled water at temp-

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TABLE I
Contact Angles of Water Drops on Copper Surfaces. (Previous studies)

Contact Angle (Degrees)	Environment	Temperature (°C)	Sample Preparation Technique	Investigator(s)
7–10	Air saturated with water vapor	room	electropolished; rinsed with water, 10%, H_3PO_4; water; ethanol	Trevoy and Johnson [17]
75	Air saturated with water vapor	25	Polished, degreased, rinsed with water	Ponter *et al.* [13]
87	Air saturated with water vapor	25	Polished, degreased, rinsed with water, stored over silica gel for 24 hours	Ponter *et al.* [4]
78, 62	Air and Steam	20	Polished, degreased	Thompson and Murgatroyd [15]
78	Air saturated with water vapor	20	not specified	Coulon [18]
60–89	Air saturated with water vapor	20	Polished	Semiczek-Szulc, Mikielewicz [19]
20–25	Nitrogen saturated with water vapor	room	Polished, degreased with soap solution	Horsthemke and Schröder [4]
10–18	Nitrogen saturated with water vapor	room	Electropolished, cleaned with water and ethanol	Horsthemke and Schröder [4]
25–60	Nitrogen saturated with water vapor	room	Rolled, degreased with soap solution immersion time 2–5 minutes	Horsthemke and Schröder [4]
10–55	Nitrogen saturated with water vapor	room	Rolled, degreased with soap solution, soaked in water at 40, 60, 90°C for up to 300 hrs. Prior to measurements.	Horsthemke and Schröder [4]

eratures of 40, 60 and 90°C for up to 300 hrs. The reproducibility was highest for surfaces which had been exposed to water at 90°C. At this temperature a uniform and homogeneous black CuO film developed while at 40 and 60°C the film was more uneven. They also examined the effect of cleaning their specimens with detergents and found that time of immersion affected the contact angle. Table I shows the contact angles of water on copper surfaces as reported by several investigators.

The mechanism of wetting on polymer surfaces is complex since not only adsorption but absorption of liquids can take place. In this study Teflon (PTFE) surfaces were used since adsorption has been reported to be low (Adam and Elliot[5]) and absorption has been observed only when using the systems cyclohexane, n-decane and n-undecane (Neumann *et al.*,[6] Boyes and Ponter.[7] To produce smooth surfaces, procedures have been described for polishing Teflon with SiC, diamond and alumina compounds (Boyes and Ponter,[8] Busscher *et al.*[9]) but this method is not now recommended because of the resulting inclusion of the polishing compound in the soft surface as microscopic study reveals. It has also been shown that pressing the samples at specific pressures and temperatures between two polished stainless steel plates results in uniformly smooth surfaces. However, oxide inclusion from the plates can be transferred to the polymer surface, and thick smooth glass plates are considered preferable. Regarding surface cleaning, little detailed information is available, the common description being degreasing with a detergent solution followed by washing consecutively in distilled water, ethanol and again distilled water before a final rinse with the test fluid as described by Boyes and Ponter.[8] From this survey it is apparent that systematic investigation to ascertain the efficacy of various cleaning agents has not been carried out, and also that satisfactory surface preparation and experimental procedures to prepare surfaces with reproducible wetting properties have not been developed.

EXPERIMENTAL

The glassware used in the experiments was washed with absolute ethanol to remove excess grease, rinsed with distilled water, then cleaned with a sodium dichromate-sulfuric acid solution before finally being irrigated several times with distilled water.

The water used was double-distilled in a device with an overflow which allowed continuous removal of the water surface. A surface tension of 72.1 dyne/cm at 25°C (which is in excellent agreement with reported values[10,11]) was measured with a Prolabo automatic tensionmeter.

All septa used were repeatedly boiled in distilled water which showed no change in surface tension at the end of the operation and all joints on the apparatus were fitted with Teflon sleeves to eliminate contamination from conventional sealants. All specimens were handled with Teflon-coated tongs which had been cleaned with a sodium dichromate—sulfuric acid solution and rinsed several times with distilled water.

The nitrogen or argon gases used were passed consecutively through an oil filter, a drying tube packed with anhydrous $CaSO_4$ and a dry

TABLE II
Contact Angle of Water Drops on Teflon Surfaces (Previous studies)

Contact Angle (Degrees)	Environment	Temperature (°C)	Sample Preparation Technique	Investigator(s)
108, 114	air	20	Not specified	Zisman [20]
128, 130	air	20–24	Pressed at unspecified pressure and temperature	Adam and Elliot [5]
108	air	25	Pressed @ 150–180°C, 500 bars	Vergara *et al.* [21]
112	air	25	Commercial grade	Dann [16]
108, 119	Argon saturated, with water vapor	20	Polished using SiC Papers and alumina compound	Boyes and Ponter [7]
98	air	19–21	Pressed @ 340°C	Hu and Adamson [22]
108	air	20	Commercial grade	Fowkes *et al.* [23]
108	Nitrogen saturated with water vapor	25	Polished using SiC Paper and alumina compound	Ponter and Yekta-Fard [24]
124	Nitrogen saturated with water vapor	25	Commercial grade	Ponter and Yekta-Fard [3]
118	Nitrogen saturated with water vapor	25	Pressed @ 200°F, 2400 Psig	Ponter and Yekta-Fard [3]

ice cold trap, and then saturated with water vapor, using a series of dispersion bottles. A microsyringe comprised of a Teflon plunger, a glass barrel and a stainless steel needle (which had been previously cleaned with absolute ethanol, then rinsed with distilled water before being dried in a clean oven) was used to form the sessile drop following Neumann and Good's procedure[12] and the advancing contact angle was measured using a telegoniometer. The observation cell was isolated from floor vibrations by thick rubber pads and care was taken to ensure that the specimens were aligned horizontally. The reported values are an average of at least four readings, and have standard deviations in the range of 0.5°–1.0°. The contact angles were reproducible to ±1°. 1.56-inch^2 specimens were cut from 99.99% copper sheeting, 1/4-inch thick. The plates were then polished consecutively with 260, 320, 400 and 600 grit silicon carbide papers while being irrigated with water. The direction of buffing was alternated through 90° for each successive grade of paper. The surfaces were polished with a rotary polisher using "Buehler AB microcloths" impregnated with 6 μm diamond paste, then cleaned in a 50:50 mixture of xylenes and methyl ethyl ketone, then absolute ethanol and polished with 1 μm diamond paste. The samples were cleaned again in a 50:50 mixture of xylenes and methyl ethyl ketone, then washed twice consecutively in absolute ethanol, and distilled water using an ultrasonic cleaner. The immersion time in each solvent was 2 minutes. All specimens were finally rinsed thoroughly with distilled water and dried with air purified by passing through a drying tube packed with anhydrous $CaSO_4$ and then through a liquid nitrogen trap. The Teflon samples of similar dimensions were prepared by two different techniques:

(a) *By polishing.* The procedure used for the copper samples was adopted except that the specimens after being polished with silicon carbide papers were degreased with a mild detergent solution, washed twice with distilled water and absolute ethanol for two minutes ultrasonically, and finally rinsed thoroughly with distilled water.

(b) *By compression.* The specimens were pressed at different temperatures and pressures between two glass plates. The surfaces were then cleaned twice consecutively in absolute ethanol and distilled water for two minutes in an ultrasonic bath and finally rinsed thoroughly with distilled water. All samples were inspected visually and with the aid of a microscope for possible scratches. All specimens were soaked in double-distilled water for a period of 24 hours to ensure that equilibrium adsorption had been established (Adam and Elliot[5]).

DISCUSSION

Contact angles of water on copper surfaces at room temperature in water-saturated argon or nitrogen atmospheres measured in the apparatus described in Figure 1 are reported in Table III. It was observed when using a detergent solution that the contact angle was markedly affected by the immersion time. Thus, when the copper specimen was immersed in the detergent solution for 15 sec., rinsed in water for 15 sec., and finally washed in ethanol for the same time, an angle of 88° ensued which is in reasonable agreement with reported values (Ponter *et al.*[13,14]), 75° and 87°, Thompson and Murgatroyd,[15] 78°). For immersion times of 2 min. the contact angle fell to 67° and when the cleaning procedure was repeated using fresh ethanol and distilled water for at least four times the contact angle dropped to 52°. This value coincides with that obtained when substituting a 50:50 mixture of

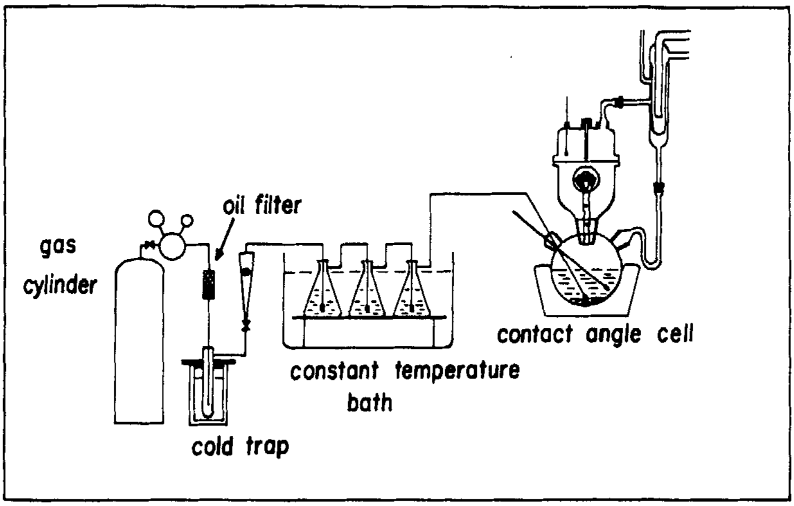

FIGURE 1 A schematic diagram of the apparatus.

xylenes and methyl ethyl ketone for the detergent. The use of this mixture is advantageous since the contact angle resulting is independent of cleaning time. It is important to note that the contact angle fell to 41° whenever the surface was polished with fresh diamond paste although an angle of 52° was again obtained when the samples were repolished using the same cloth. A microscopic examination showed that some diamond particles were imbedded in these surfaces, presumably since the fresh paste contained some sharp particles which easily penetrated the surface.

Smaller contact angles were measured (32°, 33°) when the polished copper surfaces were immersed in double-distilled water for 24 hrs. before taking measurements. It is suggested that the oxide film formed, though invisible, is responsible for this decrease since Horsthemke and Schröder[4] have observed a similar lowering effect when immersing their copper samples in water at elevated temperatures. These workers reported even lower values: 20–25° for polished surfaces, 10–18° for electropolished samples, and 25–60° for rolled samples with no further polishing. However, they did not describe the mode of polishing and therefore one cannot ascertain if surface contamination had resulted. From the above-described study it is concluded that when preparing copper surfaces, organic solvent cleaning is the most efficacious and a

TABLE III

Contact Angle of Water Drops on Copper Surfaces (This study)

Contact Angle (Degrees)	Environment	Temperature (°C)	Sample Preparation Technique
88	Nitrogen or argon saturated with water vapor	25	Polished, degreased with soap solution, rinsed twice with water and ethanol and ethanol, immersion time 15 sec.
77	Nitrogen or argon saturated with water vapor	25	Polished, degreased with soap solution, rinsed twice with water and ethanol, immersion time 30 sec.
75	Nitrogen or argon saturated with water vapor	25	Polished, degreased with soap solution, rinsed twice with water and ethanol, immersion time 1 min.
67	Nitrogen or argon saturated with water vapor	25	Polished, degreased with soap solution, rinsed twice with water and ethanol, immersion time 2 min.
52	Nitrogen or argon saturated with water vapor	25	Polished, degreased with soap solution, rinsed at least 4 times with fresh water and ethanol, immersion time 3 min.
50, 52	Nitrogen or argon saturated with water vapor	25	Polished, degreased with a 50:50 mixture of MEK/xylenes, then twice with ethanol and water, immersion time 1–3 min. samples of two different manufacturers were used.
41, 42	Nitrogen or argon saturated with water vapor	25	Using fresh diamond paste, same cleaning procedure as above.
32, 33	Nitrogen or argon saturated with water vapor	25	Same cleaning procedure as above. Samples soaked in double-distilled water at room temperature for 24 hrs.

contact angle of 52° is a reliable value for water on a smooth copper surface.

Contact angles of water on Teflon (PTFE) surfaces measured in this study at room temperature in water-saturated argon or nitrogen atmospheres are presented in Table IV. A contact angle of 130° was obtained using commercial grade PTFE, where the practice of the manufacturers is to sand polish Teflon sheets of thickness greater than 1/4 inch. For the Teflon used in this investigation this operation was omitted. For surfaces polished with SiC papers the contact angle fell to 121°, caused both by the reduction in surface roughness and the penetration of the high-energy abrasive particles into the soft polymer. To avoid inclusion of foreign particles (*i.e.* oxides) and to produce smooth surfaces, prepared 1/4-inch thick commercial samples were pressed between clean glass plates using a range of pressures and

TABLE IV
Contact Angle of Water Drops on Teflon Surfaces (This study)

Contact Angle (Degrees)	Environment	Temperature (°C)	Sample Preparation Technique
121	Nitrogen saturated with water vapor	25	Polished using SiC Papers
130	Nitrogen saturated with water vapor	25	Commercial grade—specially prepared (without normal sanding procedure)
125	Argon saturated with water vapor	25	Pressed @ 355°F, 1500 Psig
118	Argon saturated with water vapor	25	Pressed @ 355°F, 3520 Psig
117	Argon saturated with water vapor	25	Pressed @ 395°F, 7360 Psig
116	Argon saturated with water vapor	25	Pressed @ 350°F, 9600 Psig
112	Argon saturated with water vapor	25	Pressed @ 355°F, 12800 Psig

temperatures (1500–12800 psig, 350–395°F). Table IV shows that the contact angles fell from 125° to 112° with increasing pressure, the lower value being in agreement with that of Dann[16] for a commercially smooth surface. An inspection of Table II suggests that 108° is the accepted value for surfaces having very smooth finishes.

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