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Publisher *Taylor & Francis*

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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Yekta-fard, M. and Ponter, A. B.(1985) 'Surface Treatment and Its Influence on Contact Angles of Water Drops Residing on Polymers and Metals', *Physics and Chemistry of Liquids*, 15: 1, 19 – 30

To link to this Article: DOI: 10.1080/00319108508081000

URL: <http://dx.doi.org/10.1080/00319108508081000>

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Surface Treatment and Its Influence on Contact Angles of Water Drops Residing on Polymers and Metals

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(Received December 29, 1984)

Studies have been made to identify concise polishing, pressing and surface cleaning procedures for producing standard surfaces for contact angle determinations using copper and polytetrafluoroethylene (PTFE). A review of previous workers' methods and their efficacies is also reported.

INTRODUCTION

The variation of contact angle of liquid sessile drops on solids has been attributed to roughness (Wenzel¹), the static charge effect (Holly,² Ponter and Yekta-Fard³) and contamination at the solid surface or in the liquid and gaseous phases.

The scope of this paper is limited to the influence of contamination of the solid surface on the contact angle value. The contaminants can be introduced: a) in the metal or polymer during processing, b) on the surface because of chemical reaction with the environment, c) by the polishing procedure or d) because of inadequate surface cleaning.

Experiments have been carried out and are now reported to assess these

influences on the wetting of copper and polytetrafluorethylene (PTFE) surfaces by water at ambient temperature and in water-saturated atmospheres of argon or nitrogen.

A study involving copper surfaces is complex because of the chemical reaction which occurs with water and oxygen and it was decided first to survey the influence of surface and bulk contamination using gold where oxide formation is absent. (Clark *et al.*^{4,5}).

It is generally accepted that the surface of metal oxides are completely wetted by water (White⁶ and Bewig and Zisman⁷), however uncertainty arises when the wettability of oxide free metals is considered.

For examples, White⁶ claimed that an oxide-free gold surface is strongly hydrophobic but can be made hydrophilic by anodic oxidation in acid solution so that low contact angles on metal surfaces result due to the formation of oxide layers. Later White and Drobek⁸ suggested that low values of contact angle are caused by the inclusion of residual hydrophilic material from the polishing compound especially alumina. When gold surfaces were prepared by vacuum evaporation of high purity metal on silica substrates or the gold was polished with diamond abrasive followed by firing in oxygen at 1000°, contact angles between 55 and 65 degrees for water on these surfaces were reported. Electron diffraction patterns showed no contaminating oxide material.

Contact angles of water were measured by Plaksin and Bessonov⁹ on gold, silver and copper surfaces as a function of time in atmospheres of oxygen, nitrogen and carbon dioxide. In the oxygen atmosphere the contact angle of water on gold increased from 61° to 78° in 60 mins. and on silver from 52 to 68° in 30 mins. remaining constant after approximately one hour. The results with copper fluctuated due to the formation of a visible oxide film.

Under continuous condensation conditions the wettability of metals in pure steam was studied by Erb¹⁰ for extended periods of time (approx. 6 months). It was assumed that adsorbed organic surface contaminants would be removed quickly and chemisorbed contaminants after a few days. It was shown for gold (99.9% pure) that the average advancing contact angle of water was $89 \pm 3^\circ$. After three years the value fell to 65°. Radiotracer studies with oleic acid added to the refluxing water showed that the non-wetting behavior of gold was not caused by organic contamination, the average contact angle on freshly electropolished gold surfaces being $62.6 \pm 3.4^\circ$. Up to this time no account had been taken of the influence of water vapor contained in the environment on the contact angle. Erb¹¹ measured contact angles of water on gold samples treated in a number of ways. For example, for electropolished, monocrystalline gold heated in helium at 960°C, then cooled in dry helium resulted in an angle of 12–14°.

Fifteen minutes after the addition of water vapor to the helium stream a contact angle of 53 degrees was obtained. He concluded that the equilibrium contact angle of water on gold at room temperature was approximately 62 degrees, which is in agreement with the theoretical prediction of Fowkes^{12,13} and Thelen.¹⁴

Bartell and Smith¹⁵ measured contact angles of water drops on a gold surface at 25°C in a number of atmospheres and reported that in the presence of water vapor, where air was excluded, that is at low pressure, contact angles were similar, (approximately 7°) as for conditions where pure air was also present. The addition of benzene vapor caused a pronounced change in the contact angle on the gold surface, from 7° to 84°. The adsorption of benzene was not affected by the presence of air. Bewig and Zisman⁷ obtained low advancing contact angles for water on surfaces of pure gold and platinum by using a HNO₃-H₂SO₄ etching treatment which could have resulted in oxide formation on these noble metals, as suggested by White.⁶ Later Bewig and Zisman¹⁶ showed that water spread spontaneously over gold and platinum surfaces when the metals were heated to white-hot temperatures in flowing streams of high purity gases to remove adsorbed hydrophobic contaminants. They maintained that all non-zero contact angles result from contaminants of a hydrophobic nature. It should be noticed that water vapor was absent from these systems. Plumb and Thakkar¹⁷ contended that gold containing bulk impurities of as little as 1 ppm could lead to surface contamination when heated in the region of the melting point of gold. Bennett and Zisman¹⁸ then used 99.9999% purity gold to demonstrate that a drop of pure water spread spontaneously provided that strict precautions were observed to avoid any hydrophobic contamination. Observe however again that the metal surface was completely dry with no water vapor in the environment. Also it should be noted that the gold surface was polished using MgO abrasive and leached with hydrochloric acid. An examination of the surface using nuclear activation and X-ray analysis detected less than 10¹⁵ magnesium atoms/cm² and it was concluded that essentially zero MgO particles existed on the surface.

Schrader¹⁹ measured the advancing and receding contact angles of pure water on pretreated gold surfaces under conventional and ultra-high vacuum conditions. The pretreatment consisted of surface activation by heating in oxygen and then placing in a vacuum. For the conventional vacuum system, advancing angles of up to 48° were observed and for ultra high vacuum systems he again obtained high values. With the higher vacuum increasing activation resulted in a zero receding angle and for a surface treatment at 715°C for 2.5 hours followed by vacuum, produced a zero advancing contact angle. This was explained by hydrophobic contamination which was eventually removed by the ultra-high vacuum and by the

pretreatment, suggesting that the system was free of oxygen. However no consideration was paid to the presence of adsorbed water vapor which Sarakhov²⁰ has shown could only be removed completely with extreme difficulty requiring 30–40 hours evacuation at 420–450°C. With higher temperature viz: 715°C the time required to reach this condition would be much reduced and it is likely that Schrader's final experiments were carried out at this state.

Smith²¹ found that the contact angle of water on gold in an ultra-high vacuum system containing residual argon was zero, and by exposing the sample to room air for 90 min. caused the contact angle to increase to 60°. Using Auger electron spectroscopy following the measurement he detected carbonaceous contaminants. Gaines²² reported that freshly flamed gold using a soft hydrogen flame was wetted by the water, but exposure of the sample to laboratory air made the surface nonwetable. Schneegans and Menzel²³ showed that water spreads on a melted gold crystal immediately upon solidification, but not 10 min. later. Several investigators (Fowkes,^{12,13} Thelen,¹⁴ Trasatti,^{24,25,26} Clavilier and Van Hong,²⁷ Frumkin *et al.*,²⁸ and Parsegian *et al.*²⁹) studied the wetting of metals from theoretical considerations. Fowkes^{12,13} pioneered a theoretical basis for understanding the nonwetting behavior of gold by considering the dispersion-force nature of the interface between water and the oxide free metal surface from which he calculated γ_S^d to be at least 243 dynes/cm before water would spread over it. Measurements of the equilibrium spreading pressures for adsorbed vapors gave γ_S^d values for the metals copper, silver, lead, tin and iron in the range 60–108 dynes/cm. From this, Fowkes concluded that water would not spread on oxide-free metal films. Contrary to other theoretical workers, Parsegian *et al.*²⁷ suggested that gold surfaces are hydrophilic.

One can conclude from this review that the results of Erb,^{10,11} White,⁶ White and Drobek,⁸ Plaksin and Bessonov⁹ on one hand and Bewig and Zisman,^{7,16} Bernet and Zisman,¹⁸ Schrader,¹⁹ Smith,²¹ Gaines,²² and Schneegans and Menzel²³ on the other, are not contradictory but in effect represent measurements taken at different conditions, the former experiments involving gold surfaces in equilibrium with water vapor and the latter in the absence of this specie.

Using a copper surface the wetting is not only influenced by contamination as reviewed but additionally by the chemical reaction with water. Horsthemke and Schröder³⁰ measured the contact angle of water on copper surfaces which had been exposed to distilled water at temperatures 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 as seen in Table I.

The mechanism of wetting on polymer surfaces is more complex than when considering metals 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 Elliot³¹) and absorption has only been observed when using the systems cyclohexane, *n*-decane and *n*-undecane. (Neumann *et al.*,³² Boyes and Ponter³³). To produce smooth surfaces, procedures have been described for polishing Teflon with SiC,

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 ₃ PO ₄ ; water, ethanol	Trevoy and Johnson ³⁹
75	Air saturated with water vapor	25	Polished, degreased, rinsed with water	Ponter <i>et al.</i> ⁴⁰
87	Air saturated with water vapor	25	Polished, degreased, rinsed with water, stored over silica gel for 24 hours	Ponter <i>et al.</i> ⁴¹
78, 62	Air and steam	20	Polished, degreased	Thompson and Murgatroyd ⁴²
78	Air saturated with water vapor	20	Not specified	Coulon ⁴³
60-89	Air saturated with water vapor	20	Polished	Semiczek-Szulc, Mikielewicz ⁴⁴
20-25	Nitrogen saturated with water vapor	room	Polished, degreased with soap solution	Horsthemke, and Schröder ³⁰
10-18	Nitrogen saturated with water vapor	room	Electropolished, cleaned with water and ethanol	Horsthemke, and Schröder ³⁰
25-60	Nitrogen saturated with water vapor	room	Rolled, degreased with soap solution immersion time 2-5 minutes	Horsthemke, and Schröder ³⁰
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 ³⁰

diamond and alumina compounds (Boyes and Ponter,³⁴ Busscher *et al.*³⁵) but this method is not now recommended because of the resulting inclusion of the polishing compound in the soft surface as microscopic study reveals. Pressing the samples at specific pressures and temperatures between two polished stainless steel plates result in a uniformly smooth surface. However, oxide inclusion from the plates can be transferred to the polymer surface, and thick smooth glass plates are 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.³⁴ From this survey it is obvious that no systematic investigation has been carried out to either ascertain the efficacy of various cleansing agents to produce contaminant-free surfaces or experimental procedures described to provide surfaces with reproducible wetting properties. This study allows for such surfaces to be prepared.

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. Using a Prolabo automatic tensiometer, a surface tension of 72.1 dyne/cm at 25°C was obtained which is in excellent agreement with reported values.^{36,37}

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 cleaned with a sodium dichromate-sulfuric acid solution before being rinsed several times with distilled water.

The nitrogen or argon gases used were passed consecutively through an oil filter, drying tube packed with anhydrous CaSO_4 and a dry ice cold trap, then saturated with water vapor, using a series of dispersion bottles. A microsyringe comprising 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 procedure³⁸ and the advancing contact angle was measured using a telegoniometer. The observation cell was isolated from floor vibrations by thick rubber pads and care

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 ⁴⁵
128, 130	Air	20–24	Pressed at unspecified pressure and temperature	Adam and Elliot ³¹
108	Air	25	Pressed @ 150–180°C, 500 bars	Vergara <i>et al.</i> ⁴⁶
112	Air	25	Commercial grade	Dann ⁴⁷
108, 119	Argon saturated, with water vapor	20	Polished using SiC Papers and alumina compound	Boyes and Ponter ³³
98	Air	19–21	Pressed @ 340°C	Hu and Adamson ⁴⁸
108	Air	20	Commercial grade	Fowkes <i>et al.</i> ⁴⁹
108	Nitrogen saturated with water vapor	25	Polished using alumina compound	Ponter and Yekta-Fard ⁵⁰
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	

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 $\pm 1^\circ$. 1.56 inch² specimens were cut from 99.99% copper sheeting, $\frac{1}{4}$ inch thick. The plates were then polished consecutively with 260, 320, 400 and 600 grit silicon carbide papers while 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 micro-cloths' 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 CaSO₄ and then

through a liquid nitrogen trap. The Teflon samples of similar dimensions were prepared by two different techniques:

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

(b) *By compression* The specimens were pressed at difference 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 Elliot³¹).

DISCUSSIONS

Contact angles of water on copper surfaces at room temperature in water-saturated argon or nitrogen atmospheres measured in the apparatus as described in Figure 1 are reported in Table III. It was observed when using a detergent solution as the cleansing agent that the contact angle was

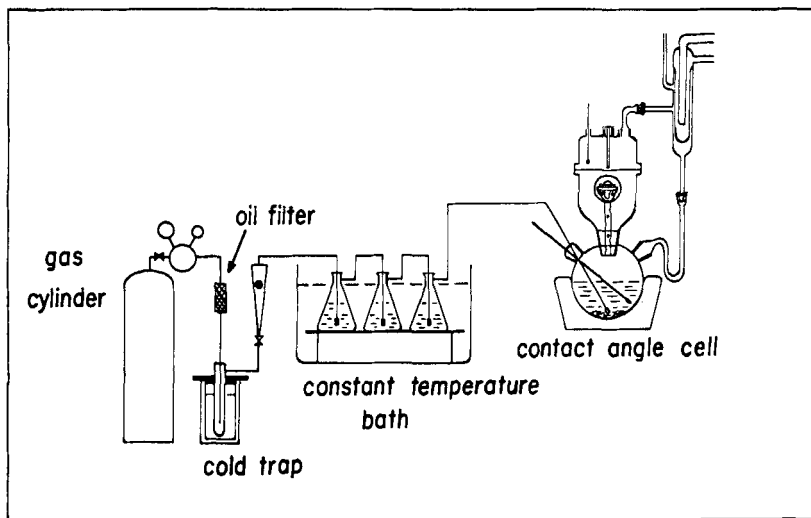


FIGURE 1 A schematic diagram of the apparatus.

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 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 1-2 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.

markedly affected by the immersion time. Thus, when the copper specimen was immersed in the detergent solution for 15 sec., rinsed by water for 15 sec., and finally washed in ethanol for the same time a value of 88° was measured which is in reasonable agreement with reported values (Ponter *et al.*,^{40,41} 75 and 87° , Thompson and Murgatroyd,⁴² 78°). For immersion times of 2 min. the contact angle dropped to 67° and when the cleaning procedure was repeated using fresh ethanol and distilled water for at least *four* times the contact angle fell to 52° . This value coincides with that obtained when substituting a 50:50 mixture of xylenes and methyl ethyl ketone instead of a detergent solution. The use of the latter mixture gave a superior cleansing action since it was found that the contact angle was independent of cleaning time. It is interesting to note that the contact angle reduced to 41° whenever the surface was polished with fresh diamond paste. However, a value of 52° was again obtained when the samples were repolished using the same cloth. A microscopic examination showed that few diamond particles were

imbedded in these surfaces, most likely because the fresh paste contained particles which easily penetrated the surface leaving the less sharp particles behind.

Lower 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 Schröder³⁰ have observed a similar lowering effect when immersing their copper samples in water at 40, 60, and 90°C for up to 300 hrs. These workers reported even lower values, $20\text{--}25^\circ$ for polished surfaces, $10\text{--}18^\circ$ for electropolished samples, and $25\text{--}60^\circ$ 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.

Contact angles of water on Teflon (PTFE) surfaces at room temperature in water-saturated argon or nitrogen atmospheres measured in this study are presented in Table IV. Contact angle of 130° was obtained using commercial grade PTFE. It is a normal practice of the manufacturers to sand polish Teflon sheets of thickness greater than $\frac{1}{4}$ inch, but this operation was omitted when producing the authors' specimens. When surfaces were polished with SiC papers the contact angle fell to 121° which is expected, since both the surface roughness is reduced and particles of the high-energy abrasive became imbedded in the soft polymer. To avoid inclusion of foreign particles (i.e. oxides) and to produce smooth surfaces, prepared $\frac{1}{4}$ inch thick commercial samples were pressed between clean glass plates

TABLE IV
Contact angle of water drops on Teflon surfaces (This study)

Contact angle (degrees)	Environment	Temperature ($^\circ\text{C}$)	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

using a range of pressures and 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 Dann⁴⁷ for a commercially smooth surface. An inspection of Table II suggests that 108° is the accepted value for surfaces having very smooth finishes.

CONCLUSIONS

The investigations indicate that when preparing polished copper surfaces for contact angle determinations, the cleansing procedure is critical. Cleaning with a detergent solution does not decrease the surface sufficiently even when followed by washing in fresh water and absolute ethanol several times. However, a 50:50 mixture of methyl ethyl ketone and xylenes effectively decreases and removes residues of the abrasive compound from the surface. Therefore, organic solvents such as those used in this study are highly recommended for cleansing polished metal surfaces. Our study reveals that copper samples polished with fresh diamond compound have higher wettability due to the presence of diamond particles on the surface. Thus the first sample polished on the polishing wheel should not be used for contact angle studies.

The study also reveals that very smooth and clean Teflon specimens are produced using high pressure and temperature when pressed between clean, thick glass plates.

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