

## WHY COPPER PREFERS INK OVER WATER

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**Abstract:** Clean copper surfaces, which exist as oxides, are hydrophilic rather than hydrophobic. With time, these surfaces become hydrophobic.

Conversion to the hydrophobic state is coincident with, but not necessarily dependent upon, oxide formation. It does depend on availability of organic contaminants.

Electrochemical potential across a copper oxide/oil/water interface has a very significant effect on development of hydrophilic or hydrophobic behavior.

These results indicate that copper's apparent hydrophobic tendency is due to a unique combination of high reactivity, appropriate electrochemistry, and availability of reactive contaminants.

### BACKGROUND

In conventional lithography, carbon-filled rubber, carbon-filled nylon, or copper are commonly used as inking rollers. These materials will continue to accept ink and ink/water mixtures under most printing conditions, including on-press locations where there is temporarily a considerable excess of dampening water. Not only are these materials oleophilic, oil-loving, but they are also hydrophobic, water-rejecting. The reasons why organic materials, such as filled rubber and nylon, have this permanent oleophilic/hydrophobic property are well-known. Reasons why copper has this advantageous property have been advanced but generally remain undocumented (1, 2).

With this background, we undertook determining why copper is oleophilic/hydrophobic in lithographic printing environments, that is, why copper prefers ink in the presence of both ink and water.

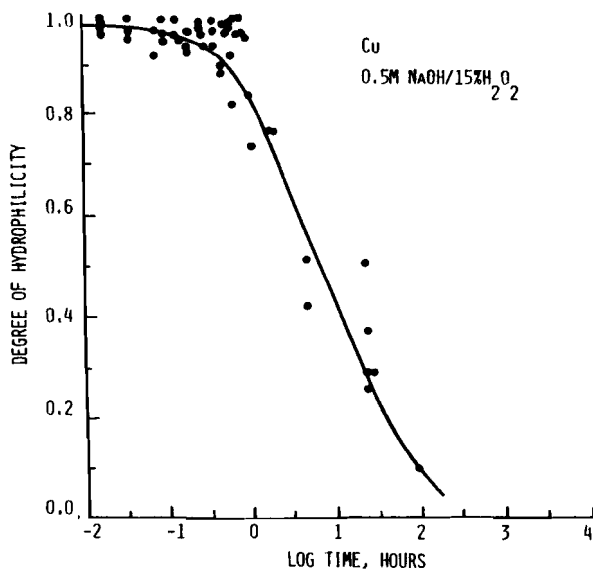
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## CLEAN COPPER SURFACES

Experiments to prepare clean copper surfaces for study showed repeatedly that freshly-prepared copper surfaces are composed of copper oxides and that they are hydrophilic, not hydrophobic. For example, Figure 1 illustrates the time dependence of the water contact angle for a polished copper surface cleaned with a sodium hydroxide/hydrogen peroxide mixture, then exposed to the laboratory environment and rinsed with deionized water. The copper became fully hydrophobic after 100 hours exposure to the laboratory environment.

FIGURE 1  
TIME DEPENDENCE OF HYDROPHILIC/HYDROPHOBIC BEHAVIOR FOR CLEAN COPPER



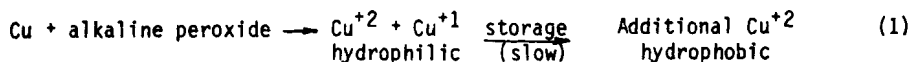
Similar experiments were performed using other treatments expected to produce different initial copper surface character. These results are summarized in Table 1. The initial water contact angles varied from about  $10^\circ$  to  $30^\circ$ .

These results clearly indicate that copper oxides are high-energy, hydrophilic/oleophilic surfaces. The differing pretreatments resulted in differing rates of auto-conversion to the hydrophobic/oleophilic condition, as indicated by the half-times  $T_{1/2}$  to reach a  $90^\circ$  water contact angle. The rate values ranged from less than 2 hours to more than 13 hours.

TABLE I  
KINETIC PARAMETERS FOR WATER CONTACT ANGLE ON COPPER

TREATMENT	pH	PREDICTED NEAR SURFACE PHASE	$\theta^0$ (H <sub>2</sub> O) DEGREES	T 1/2, HR
0.5 M NaOH/15% H <sub>2</sub> O <sub>2</sub>	10	Cu(OH) <sub>2</sub>	10	8
0.5 M NaOH	13	Cu(OH) <sub>2</sub>	21	5
0.5 M NaOH/Na <sub>2</sub> SO <sub>3</sub>	13	Cu(OH) <sub>2</sub>	25	5
BORATE BUFFER (-650 MV)	8.5	Cu <sub>2</sub> O	25	5
BORATE BUFFER (-193 MV)	8.5	Cu(OH) <sub>2</sub>	23	13
0.1 M HNO <sub>3</sub> (pH ADJ)	2.4	n.o.	32	4
0.1 M CITRIC ACID	2.4	Cu <sub>2</sub> O	30	1.7

Our analysis of these copper surfaces confirmed that the Table I predicted oxides (3,4) are indeed present initially. Copper is far too reactive chemically to exist under ordinary conditions as the unoxidized metal. The changes in copper oxide formation during copper's conversion from hydrophilic to hydrophobic may be summarized by Equations (1) and (2):



Clearly, exposure of clean, oxidized copper to the environment involves further oxidation to the Cu<sup>+2</sup> state, and coincidental appearance of hydrophobic/oleophilic behavior. The question is whether the two results are related.

### SURFACE FILMS FORMED BY COPPER

The persistence and stability of this hydrophilic to hydrophobic behavior of copper surfaces was assessed by exposing clean copper specimens to a variety of environments. Water contact angles and oxide thicknesses were determined as a function of time. The latter were determined using cyclic voltametry, a simple but selective technique allowing separate determination of Cu<sup>+1</sup> or

$\text{Cu}^{+2}$  oxidation state film thicknesses (Appendix I). Oil contact angles were not determined to avoid disturbing the surfaces with additional contaminants.

The copper surfaces were abraded with 600 grit SiC paper and treated for five minutes each, first in an alkaline peroxide solution (0.5M NaOH/15 percent  $\text{H}_2\text{O}_2$ ), then in 0.1M citric acid solution. The samples were then placed in one of the following environments for varying periods of time:

1. Room air at 45 percent relative humidity (RH).
2. A controlled chamber containing filtered room air at either 0 percent RH, 45 percent RH, or 90 percent RH.
3. A similar chamber at 45 percent RH, containing  $\text{N}_2$ .
4. Oleic acid.

Details of the experimental procedures are given in Appendix I. Figures 2 and 3 show the time dependence for growth of the  $\text{Cu}^{+1}$  and  $\text{Cu}^{+2}$  oxides at the three different relative humidity conditions in the controlled chamber.

FIGURE 2  
OXIDE (I) THICKNESS ON COPPER AS A FUNCTION OF TIME  
AT VARIOUS HUMIDITIES

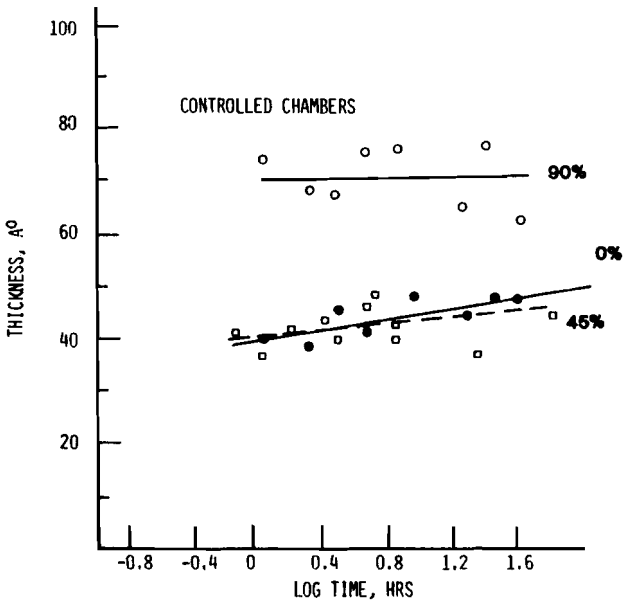
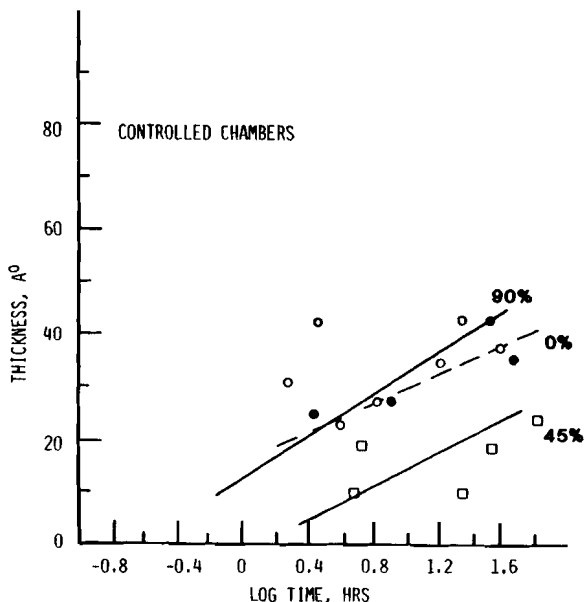


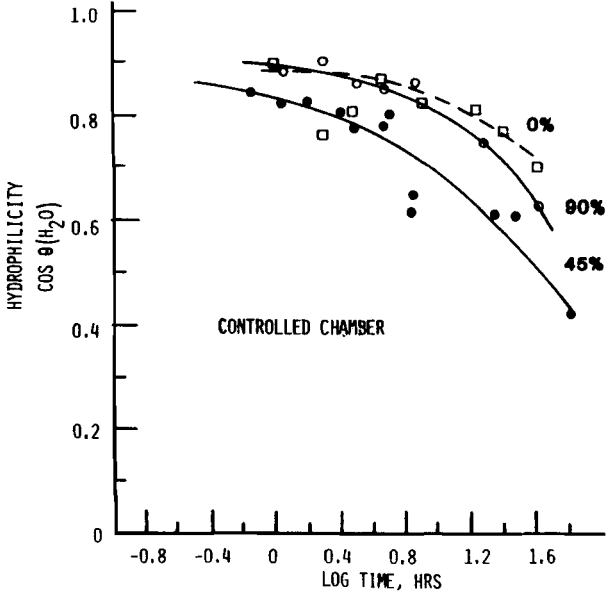
FIGURE 3  
OXIDE (II) THICKNESS ON COPPER AS A FUNCTION OF TIME  
AT VARIOUS HUMIDITIES



A thick  $40\text{Å}^\circ$  to  $70\text{Å}^\circ$   $\text{Cu}^{+1}$  oxide is already present at the first measurement time, about 20 minutes. Subsequent growth is slow to nil under these experimental conditions. However,  $\text{Cu}^{+2}$  oxide growth begins after about one hour and proceeds at a rate dependent upon the moisture content of the air, achieving a thickness of from about  $20\text{Å}^\circ$  to  $40\text{Å}^\circ$ .

The rates at which these surfaces become hydrophobic are shown in Figure 4 as plots of  $\cos \theta$  (water contact angle) versus logarithm of time. The quantity  $\cos \theta$  is proportional to the energy of interaction of water with the surface and is, therefore, a measure of hydrophilicity. The times,  $T_{1/2}$ , to reach a  $\cos \theta$  value of 0.5, were estimated at 160 hours, 40 hours, and 65 hours for the 0, 45, and 90 percent RH conditions, respectively. Obviously, the onset of hydrophobic behavior (low  $\cos \theta$  values) for copper in a dry environment is significantly longer than in wet environments. This fact is coincident with the slower  $\text{Cu}^{+2}$  oxide growth rate of Figure 3 under the dry condition.

FIGURE 4  
 WATER CONTACT ANGLE AS A FUNCTION OF TIME  
 FOR COPPER AT VARIOUS HUMIDITIES



Similar data for copper exposed to room air at 45 percent RH are compared in Figures 5 and 6 with the 45 percent RH controlled air.

FIGURE 5  
 OXIDE THICKNESS ON COPPER AS A FUNCTION OF TIME  
 AT 45% RELATIVE HUMIDITY

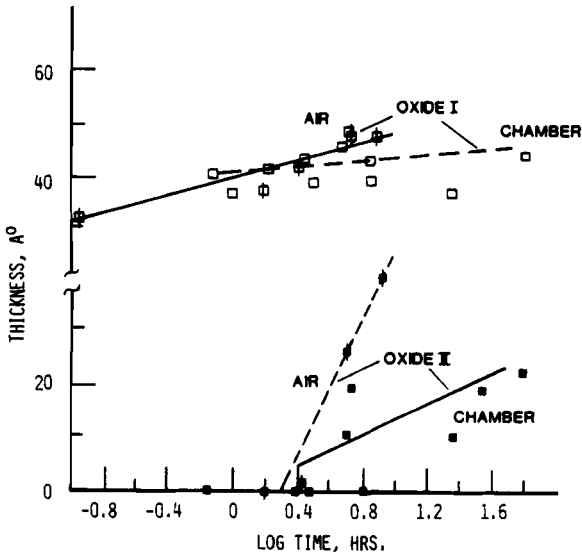
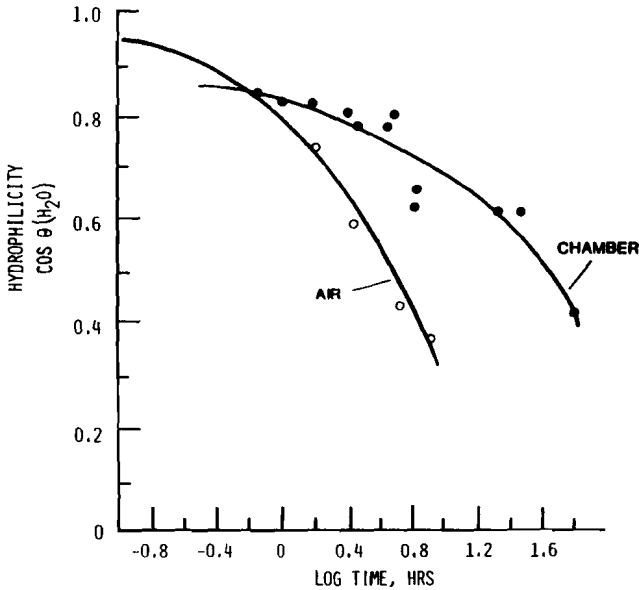


FIGURE 6  
 WATER CONTACT ANGLE AS A FUNCTION OF TIME FOR COPPER  
 AT 45% RELATIVE HUMIDITY



The  $T_{1/2}$  value for conversion to oleophilic nature is an order of magnitude lower for the room air condition, about 3.5 hours compared with 40 hours for the controlled environment. And, the  $Cu^{+2}$  oxide growth rates are similarly disposed. Apparently, the controlled chamber filtered air contains a significantly lower concentration of organic contaminants.

Under nitrogen atmosphere conditions, no  $Cu^{+2}$  growth occurs, Figure 7. Hydrophobic surface formation takes place, Figure 8, but at a slow rate. The  $T_{1/2}$  value is about 100 hours with reduced concentrations of both oxygen and organics.

These data infer that oxide growth influences the development of oleophilic/hydrophobic behavior but that oxide growth alone does not determine preference of the surface for oil over water.

FIGURE 7  
OXIDE THICKNESS ON COPPER AT 45% HUMIDITY IN NITROGEN

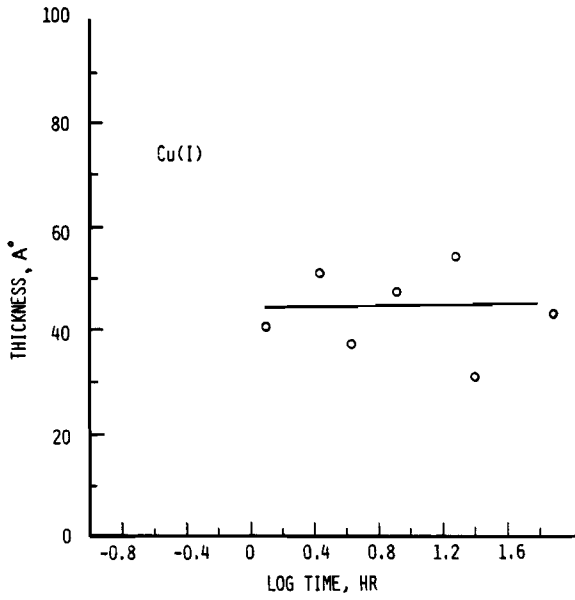
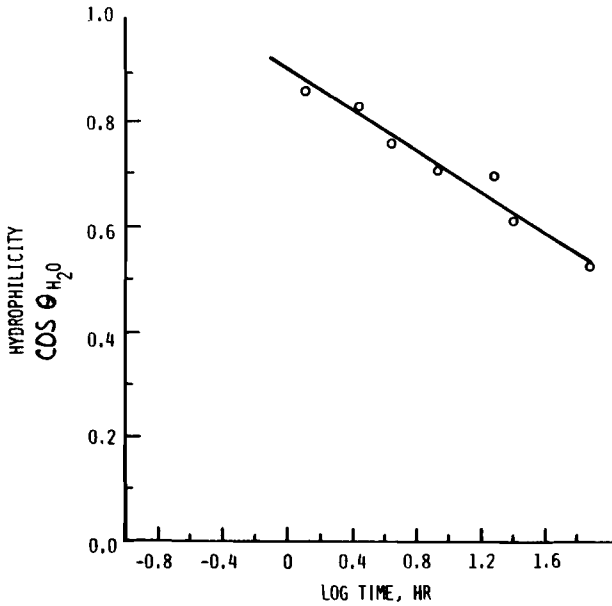


FIGURE 8  
WATER CONTACT ANGLE ON COPPER AT 45% HUMIDITY UNDER NITROGEN





Exposure of the fresh copper oxide surface to oleic acid converts it to a hydrophobic surface with no evidence of  $\text{Cu}^{+2}$  growth, as shown in Table II. In fact if  $\text{Cu}^{+2}$  is initially present, the  $\text{Cu}^{+2}$  oxide gradually disappears upon exposure to oleic acid.

These data suggest the formation of a complex with oleic acid, an observation confirmed by electron-spin-resonance analysis of an oleic acid solution left in contact with copper. An oleic acid soluble complex was formed; but, in addition, a relatively permanent hydrophobic surface was also formed.

TABLE II  
INFLUENCE OF OLEIC ACID ON COPPER OXIDE FILMS

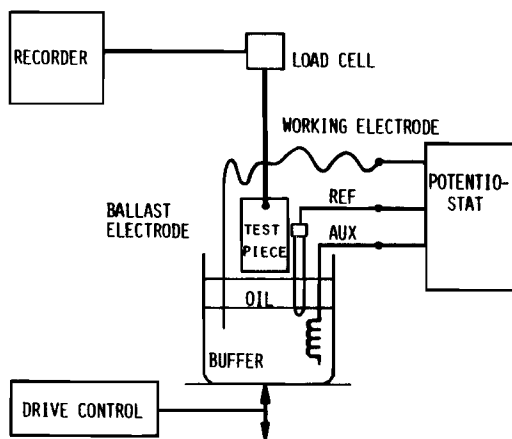
COPPER PRETREATMENT	TIME IN OLEIC ACID (HOURS)	OXIDE THICKNESS ( $\text{Å}^0$ )		WATER CONTACT ANGLE (DEGREES)
		Cu(I) OXIDE	Cu(II) OXIDE	
ALKALINE PEROXIDE AND CITRIC ACID	0.25	11	0	95
	1.0	14	0	90
	140	± 5	0	96
ALKALINE PEROXIDE	0.25	103	5	104
	1.0	77	4	97
	95	± 1	0	90

## ELECTROCHEMICAL INFLUENCES ON WETTABILITY

Considerable evidence exists to substantiate that wetting or nonwetting of metals by oil in the presence of water is the result of corrosive chemical interaction at the water/oil/metal interface. Corrosion is an electrochemically driven process, which fact prompted examining electrochemical influences on copper wettability by oil and by water.

A Wilhelmy balance (7), Figure 9, was constructed to allow direct measurement of wetting force (tension) encountered as a copper coupon is passed from air through

FIGURE 9  
MODIFIED WILHELMY BALANCE



oil and into buffered water representing dampening solution. The Wilhelmy Balance was modified to allow applying an electrochemical potential between the test piece and the aqueous solution.

It can be shown that the force on the metal coupon relates to the angle that the water/oil interface forms at the metal surface. A simple model of the system results in a general equation for any one of the changes in force,  $f$ , going from one liquid to the other:

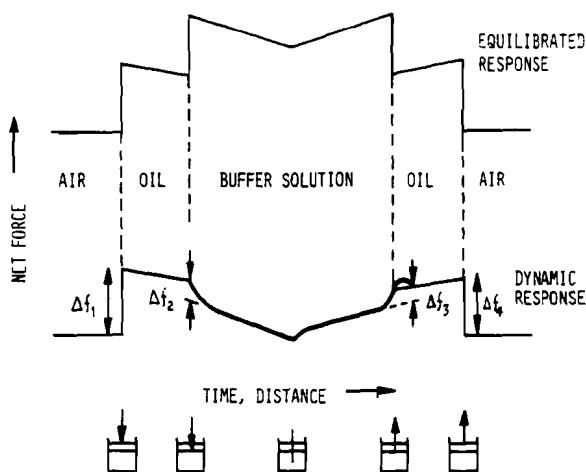
$$\frac{f}{P} = \gamma_{os} \cos \theta$$

where  $P$  is the perimeter of the coupon and, in this example,  $\gamma_{os}$  is the dynamic surface tension at the oil/water-solution interface and  $\theta$  the interfacial contact angle. The important practical point is that we can measure  $f$  using the Wilhelmy balance, and  $P$  is a constant factor. This allows direct calculation of the quantity  $\gamma_{os} \cos \theta$ , which value approximates the interfacial force operating on the copper coupon.

Large positive values of  $\gamma_{os} \cos \theta$  correspond to an oleophilic surface response, that is, the net force on the coupon is towards the oil phase, due to wetting interaction. Negative values of  $\gamma_{os} \cos \theta$  indicate hydrophilic surface response, the net force being towards the aqueous phase and is due to water wetting the coupon.

Experimental procedures are outlined in Appendix II. The force response during the time a coupon traverses at a constant rate from air into oil then into water and out again is illustrated in Figure 10. The upper illustration represents the response expected at infinitely-slow traverse time. A typical actual response is shown in the lower portion of Figure 10, illustrating hysteresis encountered because of the dynamic nature of the experiments. The dashed lines correspond to extrapolations made to obtain force values unencumbered by hysteresis.

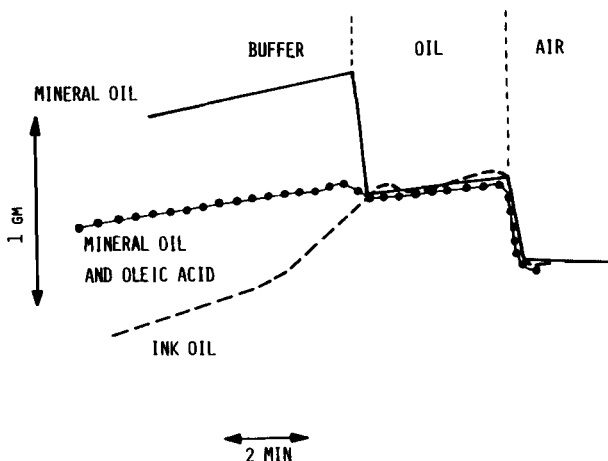
FIGURE 10  
SCHEMATIC OF WETTING FORCE TEST RESULTS



Our best results were obtained using the withdrawal portion of the cycle. And Figure 11 illustrates typical print-out curves for aqueous buffer/mineral oil conditions, for aqueous buffer/ink oil conditions and for aqueous buffer/mineral oil plus oleic acid conditions (8).

Withdrawal of the copper specimen from the aqueous phase to the mineral oil phase corresponds to near-ideal (solid line) force/time curve behavior. The negative net force values indicate the very hydrophilic and oleophilic nature of copper in the absence of any specific chemical interactions with the liquids. Clean copper, being a high energy surface, is wetted by the oil or the water, depending upon the medium it is in.

FIGURE 11  
WITHDRAWAL FORCES ON COPPER AT OIL/WATER INTERFACE  
AS A FUNCTION OF OIL TYPE

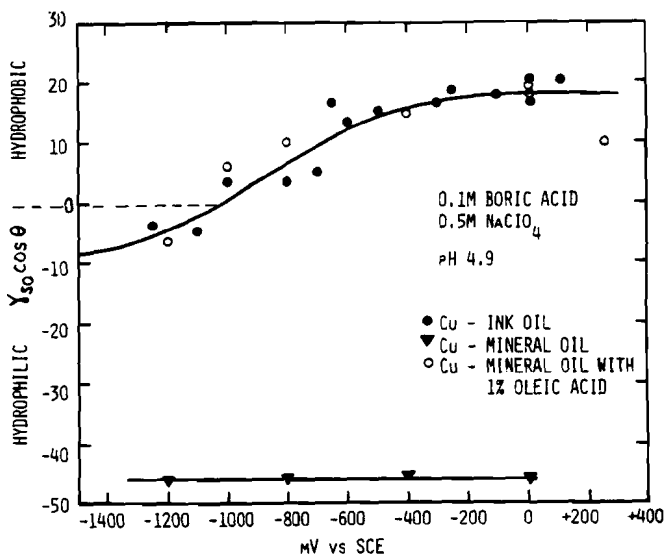


When ink oil is substituted for mineral oil, dashed curve of Figure 11, the sign of the  $\Delta f_2$  and  $\Delta f_3$  values change from positive to negative. Clearly, some kind of interaction had taken place prior to or at the water/oil interface that negates wetting of the copper by water.

When one percent oleic acid is added to mineral oil, the force response is similar to that when ink oil is used, dotted line of Figure 11. Separate experiments clearly showed that reaction with an active compound is involved. Placing a copper specimen in the aqueous solution without first passing through the oleic acid/mineral oil upper layer, gave the typical Figure 10 (upper curve) hydrophilic response upon withdrawal. This should be compared with the hydrophobic response, Figure 11, obtained when the copper is first passed through the oil phase.

With these experiments as background, we investigated the electrochemical potential influence on the oleophilic behavior of copper. The results are summarized in Figure 12.

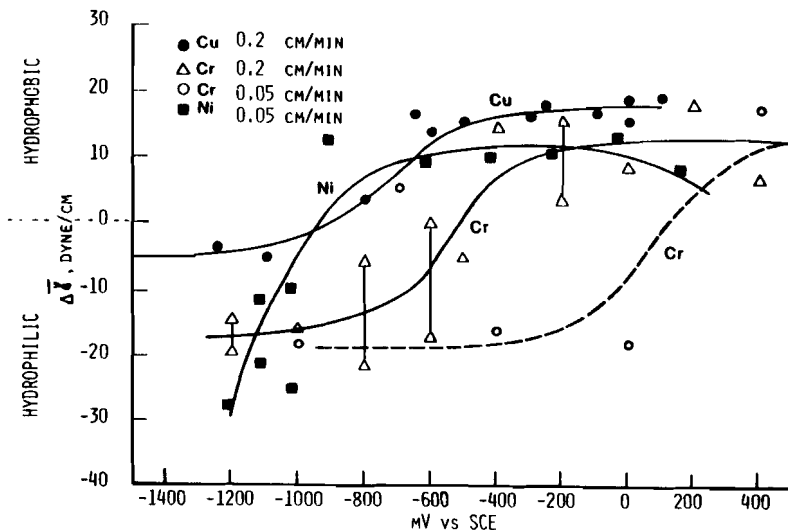
FIGURE 12  
 DEPENDENCE OF COPPER HYDROPHILICITY ON ELECTROCHEMICAL POTENTIAL  
 ACROSS OIL/SOLUTION INTERFACE



It is apparent that the copper surface changes from oleophilic to hydrophobic as the electrochemical potential becomes less negative. The changeover value is about -800 mV. On the other hand, the absence of a reactive component in the mineral oil, negates appearance of any electrochemical effect. This is shown in the lower curve of Figure 12 representing mineral oil without additive. These results strongly suggest that the hydrophobic behavior of copper is electrochemical in nature, but that it also requires a reactive contaminating species, such as organic acids, unsaturated oils, alcohols, and the like. Such species are usually present in normal air environments. And, if not, copper is known to be an active catalyst for chemical reactions. It probably can convert many carbonaceous materials to reactive hydrophobic entities at its surface at room temperature.

Separate experiments with nickel and chromium verified that these results are not peculiar to copper. Figure 13 demonstrates that at sufficiently negative potential copper, chromium or nickel are hydrophilic. At sufficiently positive potential, each can become hydrophobic. The dashed line curve for chromium represents a slow withdrawal rate and likely represents more realistic values than the solid line chromium curve.

FIGURE 13  
WILHELMY BALANCE RESULTS FOR VARIOUS METALS



### CONCLUSIONS

1. Copper surfaces initially exhibit hydrophilic/oleophilic properties, if suitably cleaned, regardless of the oxidation state of the surface oxide film.

2. Exposure of clean copper surfaces to ordinary environments renders the copper hydrophobic/oleophilic. This change is coincident with increase in the  $\text{Cu}^{+2}$  oxide content in the surface.

3. Under nitrogen atmosphere conditions, the hydrophobic transformation takes place slowly and no  $\text{Cu}^{+2}$  formation occurs, indicating that oxide formation, while perhaps helpful, is not essential to the transformation.

4. Organic acids readily attack  $\text{Cu}^{+2}$  oxide, suggesting that conversion of  $\text{Cu}^{+2}$  oxide to a thin layer of organo-copper complex occurs in air due to presence of environmental organic materials. The resulting surface is hydrophobic.

5. The application of a sufficiently cathodic electrochemical potential destabilizes the oleophilic phase formed on copper by reaction with organic compounds. Under these conditions, the copper reverts to oleophilic/hydrophilic and water can then readily debond the ink from the copper surface. This result is readily demonstrated by simply switching from a more positive to a more negative potential.

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## APPENDIX I

### ELECTROCHEMICAL DETERMINATION OF THE SURFACE PHASES ON COPPER

Flag-shaped copper coupons were abraded with 600 grit SiC and placed in a 0.4 M NaOH/4.5 percent H<sub>2</sub>O<sub>2</sub> solution for 5 minutes followed by a thorough rinse in deionized water, and treated for 5 minutes in an 0.1 M citric acid solution. The coupons (7 cm<sup>2</sup>) were immersed in 0.1 M H<sub>3</sub>BO<sub>3</sub>/0.5 M NaOH buffer (pH 9.2) which had been flushed with Ar for 40 minutes. The potential of the Cu coupon was varied at a constant rate of -10 mV/s from the open-circuit potential to -1000 mV vs SCE (saturated calomel electrode) using a sweep generator and a potentiostat connected to a Pt wire counter electrode and a SCE reference electrode. The Cu coupon served as the working electrode. The current vs voltage response was recorded on an x-y recorder. Integration of the area under the current vs voltage (time) curve provided a measure of total charge, Q, passed. The oxide thickness,  $\delta$ , can be determined according to the equation

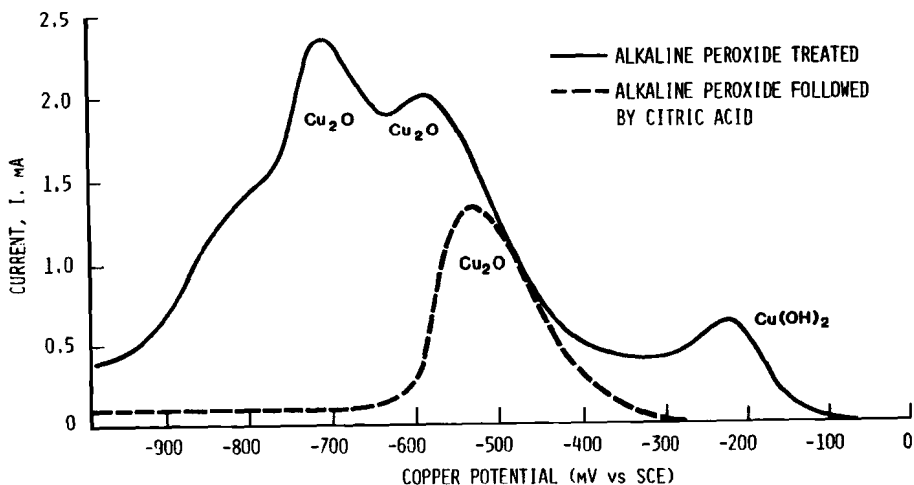
$$\delta = \frac{V Q}{2F}$$

where V is the molar volume of Cu<sub>2</sub>O, CuO or Cu(OH)<sub>2</sub>, Q is the charge/cm<sup>2</sup> and F is the electrochemical equivalent (96487 coulomb/equivalent).

Figure I-1 shows the current vs voltage, results for copper coupons treated in the alkaline peroxide (solid line), and for copper coupons treated in the alkaline peroxide followed by exposure for 5 minutes to 0.1 M citric acid (dashed line). The current maximum near -200 mV corresponds to the reduction of Cu<sup>+2</sup> species (most likely Cu(OH)<sub>2</sub>) during voltametry testing, and the two current maxima near -600 mV result from the reduction of Cu<sub>2</sub>O. The second and third maxima at ca -600 and -700 mV and a shoulder at -800 mV, probably represent the reduction of several kinetically inequivalent Cu<sub>2</sub>O sites. Significantly, only a peak at -540 mV occurs for the citric acid treated specimen due to reduction of only one available Cu<sub>2</sub>O site. The citric acid treatment eliminates the Cu<sup>+2</sup> species on the surface and the kinetically inert Cu<sup>+1</sup> species in the reduction cycle.

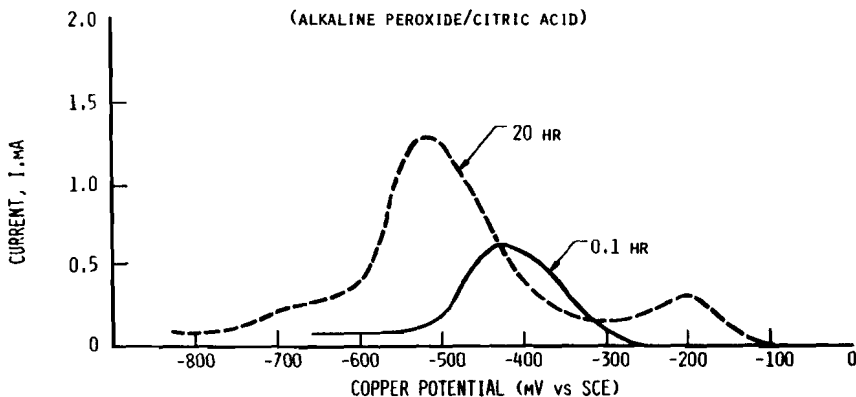


FIGURE I-1  
VOLTAMMETRIC REDUCTION CURVES FOR Cu PRETREATED WITH COPPER



As noted in this report, freshly prepared Cu exhibits relatively hydrophilic behavior. However, in time, the surface converts from hydrophilic to oleophilic. Figure I-2 shows the cathodic curves for two copper specimens treated in alkaline peroxide followed by an 0.1 M citric

FIGURE I-2  
VOLTAMMETRIC REDUCTION CURVES FOR Cu,  
PRETREATED COPPER INITIALLY AND AFTER 20 HRS.  
(ALKALINE PEROXIDE/CITRIC ACID)



acid treatment. The dashed curve presents the results for the specimen which had aged for 20 hours and had a water contact angle of  $60^\circ$ . The solid curve presents the results for the initial state having a water contact angle of  $20^\circ$ . At the initial time, the copper showed only Cu(I) species to be present. Integration of the charge passed revealed that the initial film was  $15\text{\AA}$  thick. After 20 hours the  $\text{Cu}^{+1}$  film had more than doubled

to give a value of  $38\text{\AA}$ , and the onset of a current peak at  $-200\text{ mV}$  revealed the presence of a  $\text{Cu}^{+2}$  film having a  $3\text{-}7\text{\AA}$  thickness.

The oxidation state and extent of the  $\text{Cu}_2\text{O}$  film formed by the alkaline peroxide can be determined with a great deal of sensitivity using this technique. This approach for determining film thickness was tested by comparing the thickness results for a highly polished Cu specimen ( $1\ \mu\text{m}$  finish) treated in alkaline peroxide to the thickness determined by the well established but tedious ellipsometric technique. An electrochemically determined film thickness of  $77\text{\AA}$  corresponded to an ellipsometric estimate of  $60\text{\AA}$ .

## APPENDIX II

### MEASURING SURFACE FORCES AT THE COPPER/OIL/WATER INTERFACE

Figure 9 shows a schematic of the apparatus used for the potentiostated surface force measurements. An Instron bench-top testing machine and a BC 1200 potentiostat comprise the instrumental portion of the system. The Instron provides a programmed drive to a 15 cm diameter x 7.5 cm deep beaker resting on the cross arm. The beaker contains an auxiliary electrode (AUX), a reference electrode (REF), and a ballast electrode immersed in 450 ml of a buffer solution under a 150 ml layer of oil. The ballast electrode was connected to the test specimen which was suspended from a 5 gm load cell. These electrodes were connected to the working electrode input of the potentiostat. The ballast electrode allowed the specimen to be either in or out of the buffer solutions without open-circuiting the potentiostat. The potentiostat maintained the test piece at a control potential with reference to the saturated calomel reference electrode (SCE) by passing an appropriate current to the test specimen through the auxiliary electrode. A thin, 0.015 cm diameter, copper wire connected the specimen to the potentiostat. The wire was sufficiently light in order to minimize any extraneous forces on the specimen.

The aqueous phase contained 0.1M boric acid ( $H_3BO_3$ , Baker reagent, lot No. 402476). In addition, the solution was made 0.5 M in sodium perchlorate ( $NaClO_4 \cdot H_2O$ , G. Frederick Smith, Lot No. C3). The boric acid provided a pH buffer which eliminated any localized variations in pH in the aqueous phase as a result of electrochemical reactions. The inert, neutral, and non-complexing  $NaClO_4$  electrolyte lowered the resistivity of the aqueous phase, thereby optimizing the "throwing-power" of the potentiostatic control. This solution has a pH of 4.9. Making the solution 0.05 M in NaOH provided a pH 9 buffer.

A Flint ink oil (03-8040) and reagent grade light mineral oil (Sargent-Welch viscosity 80-90 cp at 100 F) were used for the experiments. For several experiments, oleic acid (Apache Chemicals, Inc.) was added to the mineral oil.

The Cu specimen was a 7.76 cm wide by 0.026 cm thick

sheet of OFHC copper giving a perimeter of 15.5 cm. The specimen was polished with 600 grit SiC paper, rinsed in distilled water and immersed for 5 minutes in 0.1 M citric acid, rinsed again in distilled water and dried in a stream of N<sub>2</sub>. Care was taken to abrade the edges as well as the surface of the specimen.

## Results

Figure 10 schematically presents typical force vs time responses for copper penetrating into and retracting from the non-reactive mineral oil/solution (ph 4.9) interface and a reactive-oil (ink oil)/water interface. Considering the case for an inert oil, a positive force into the liquid appears as a discontinuity in the force-time curve as the specimen touches the oil. Assuming a 180° contact angle at the oil/metal interface,  $\Delta f_1/P$  will equal  $\gamma_{OM} - \gamma_O$ . As the specimen pushes through the oil, a buoyant force proportional to the depth causes a downward sloping force vs time curve. As the metal specimen traverses the inert-oil/solution interface, an additional sharp increase in force toward the liquid occurs as a result of the hydrophilic interaction of the metal surface with the aqueous phase. This force divided by the perimeter,  $\Delta f_2/P$ , equals  $\gamma_{OS} \cos \theta$  and is proportional to  $\gamma_{SM}$ . Upon reversing the drive, the forces in the inert-oil/solution system reverse as shown in Figure 10. In the case that a specific reaction of the metal with the oil occurs, the formation of the meniscus at the interface will depend on time, and hysteresis occurs. The magnitudes of the changes of force going from oil to solution,  $\Delta f_2$ , and from solution to oil,  $\Delta f_3$ , are not equal. Strictly speaking, thermodynamic quantities such as surface tension cannot be defined for dynamic systems such as these. Nevertheless, dynamic functions may be operationally defined from the extrapolated values,  $\Delta f_2$  and  $\Delta f_3$ :

$$\frac{\Delta f_2}{p} = \bar{\gamma}_{OS} \cos \theta = \frac{(\bar{m}_O - \bar{m}_S) 980.66}{p}$$

$$\frac{\Delta f_3}{p} = \bar{\gamma}_{SO} \cos \theta = \frac{(\bar{m}_O - \bar{m}_S) 980.66}{p}$$

where  $m_i^>$  and  $m_i^<$  refer to the loads needed for the respective advancing and receding movements of the specimen across the interface to balance the force pulling the specimen into the fluid at phase  $i$ , as extrapolated to the point in time when the three-phase junction (metal, oil, water) first forms. The broken lines in Figure 10 shows the extrapolation. The acceleration due to gravity,  $980.66 \text{ cm/sec}^2$  scales the results to units of force in dynes.