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Evaluation of electrical contact materials for mercury switches designed to detect angular rotation

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The adherence of mercury to a variety of materials was evaluated for various surface treatments in terms of contact angle and maximum meniscus height on separation. It was found that arcing markedly increased wettability and that roughening produced mercury repellent surfaces.

1. Introduction

Mercury adheres to most metals and metal oxides [1, 2] such that a mercury bridge or meniscus is formed on separation. For mercury switches designed to detect rotation, the minimum detectable angular change ϕ is determined by the maximum lateral meniscus length (chord length c) between mercury and small electrical leads inserted radially a small distance into a spherical cavity of radius R. The relationship between these geometrical parameters is expressed in Equation 1 [3] and shown in Fig. 1 with typical values for the case where the axis of rotation passes through the centre of the switch cavity.

$$c = 2R \sin(\phi/2) \qquad (1)$$

In order to improve either sensitivity or miniaturization, electrically conductive materials which exhibit the least adhesion to mercury are required. The results of a search for and comparison of such materials are reported below.

2. Experimental details

Measurements of maximum mercury meniscus height at break were made in a glass vacuum chamber bearing an electrical feedthrough and sample mounting fixture at the top, a mercury manometer at the bottom, and a side tube leading directly to a three stage diffusion pump. The mercury reservoir at the base of the manometer column was mounted on a micrometer such that the mercury level in the chamber could be gently raised or lowered to make or break contact with the lower ends of vertically mounted sample rods. The mercury surface, meniscus, and sample end were back lighted and observed through the chamber walls using a microscope which replaced the input optics of a video camera. Dynamic mercury-sample make/break contacting was viewed at about 20 × magnification on a cathode-ray tube (CRT) video display and stored for play back using a TV video tape recorder. A 5 litre vacuum reservoir was mounted between the mercury diffusion pump and a mechanical pump and was provided with valves for back-to-air and for sealing the system. The mechanical pump could be turned off and diffusion pumping continued into the reservoir. This mode of operation avoided vibration from the mechanical pump. Isolation from building vibrations (essential for these measurements) was achieved by increasing the mass of the system to about 1 tonne using lead ingots and raising the entire apparatus on air mounts.

In situ 10 min cleaning of the sample rods was performed in a 1 kW r.f. mercury plasma within the 1 in. (25 mm) diameter vacuum chamber between the sample and boiling mercury surface induced by an externally mounted, water cooled pancake coil. The sample rods were negatively biased with respect to the grounded mercury pool at a controlled potential chosen in the range 0–5 kV d.c.

Mercury sessile drop contact angle measurements in air were also made on flat plate samples which were ultrasonically solvent cleaned followed by cleaning in an argon r.f. plasma (15 min, 150 W, 0.6 torr). The standard deviation of the average of six contact angle measurements was consistently less than $\pm 1°$.

3. Results and discussion

The adherence of mercury to electrical contacts is responsible for the meniscus observed on separation, and, as mentioned in Section 1, the maximum meniscus length is of primary interest in the design of mercury switches for sensing angular rotation. In order to relate our measurements of maximum meniscus height to the measurements of others, we also measured the contact angles for mercury drops resting on the solids (Fig. 2). There is a relationship between the two since the work of adhesion (W°_{SL}) is the product of force and meniscus height and can be expressed in terms of the contact angle (θ) and the work of cohesion of the liquid (W_c) [4].

$$W^{\circ}_{SL} = (1 + \cos\theta) W_c/2 \qquad (2)$$

It is a common concept that "if the contact angle is greater than 90°, the liquid is considered not to wet the solid — in such a case drops of liquid on the solid tend to move easily about on the surface . . . " and the "liquid will tend not to enter a capillary constructed of

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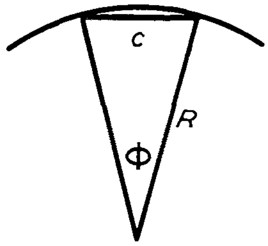

$$c = 2R\sin(\phi/2)$$

Figure 1 For a switch cavity diameter $2R = 0.25$ in. and a maximum mercury meniscus length $c = 0.015$ in., the minimum detectable rotation is $\phi \sim 7°$. Conversely, for fixed sensitivity, the meniscus limits miniaturization.

the solid. On the other hand, a liquid which wets a solid is considered to have a zero contact angle" [4]. These statements are sometimes misconstrued as indicating extremes in wetting or non-wetting behaviour with sharp differentiation at $\theta = 90°$, to the point of generating misleading terms such as "wetting angles" ($\theta < 90°$) and "non-wetting angles" ($\theta > 90°$). The truth of the matter is that wetting is a continuously variable phenomenon between $\theta = 0$ and $180°$.

We found that mercury drops about 1 mm in diameter resting on metal oxide surfaces exhibited contact angles between 115 and 155°, depending on the type of oxide, yet adhered so strongly that the drops were not displaced by gravity on rotating the solids to a vertical position. This behaviour is readily understood from Equation 2 and Fig. 3, a plot of $1 + \cos\theta$ (a term proportional to the work of adhesion) as a function of the contact angle θ. It should be noted that $1 + \cos\theta$ has only positive values for all possible contact angles (0 to 180°) and that the curve is monotonic with no discontinuity at $\theta = 90°$. One must conclude that "wetting" or "non-wetting" and "adherent" or "non-adherent" are relative terms and a matter of measurable degree.

We found that all of the materials investigated for which mercury–solid contact angles were between 115 and 170° exhibited positive menisci on separation. The maximum meniscus heights were approximately 6/10 of the diameters of the rods over a range from 1/100 to 1/16 in. As shown in Fig. 3 and Table I, these materials included oxides, carbides, borides, chlorides and hydrides. Most of the oxides were thin coatings such as are normally present on metallic samples polished in air, ultrasonically solvent cleaned, followed by argon plasma cleaning. If the coatings are removed from the surfaces in the presence of mercury by any

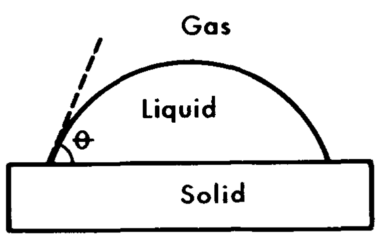

Figure 2 The contact angle θ of a drop resting on a surface in an inverse function of the adhesion of the liquid to the solid.

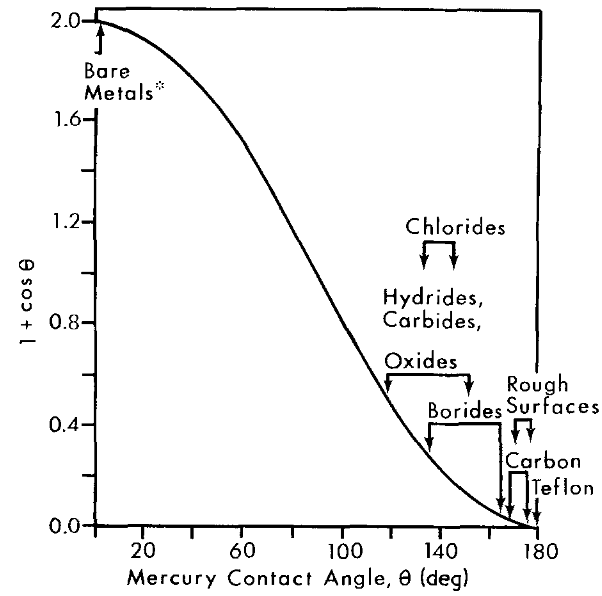

Figure 3 The work of adhesion W_{SL} is a function of the contact angle θ between mercury and a solid and the work of cohesion W_c of the mercury, where $W_{SL} = (1 + \cos\theta)W_c/2$. The various types of solids investigated fall in the bands indicated by the arrows. *The wetting of bare metals by mercury was reported in [1] and [2].

means such as thermal decomposition or spalling, reduction in hydrogen, mercury ion bombardment in an arc or plasma, electrical breakdown, or mechanical abrasion, then the metallic substrates are wetted by mercury (we measured contact angles less than 10° after multiple break type arcs at 10 V and 0.3 A and 0–2° after sputtering has been reported by others [1]). After arcing the meniscus height at contact separation increased significantly, and some metals and alloys were then subject to corrosion, electrolytic attack, dissolution, or embrittlement by mercury. It has been reported that arc protection circuits do not eliminate arcing when both contact opening and closing arcs occur, but do limit the arc energy thus reducing

TABLE I Mercury contact angles on argon plasma cleaned materials

Material	Contact angle (deg)
Nitrogen, iron, molybdenum, tungsten, platinum, silver, copper	0–2
Oxide on chromium (oxygen plasma, shiny)	115
Oxide on silicon	118.5
Oxide on tantalum	122.5
Titanium dioxide (transparent)	126.5
Titanium carbide	126.5
$FeCl_2 \cdot 4H_2O$	132.5
Oxide on titanium diboride (violet)	135
Oxide on chromium (u.v./O_3, brown)	135.5
Oxide on tungsten	137.5
Amorphous silicon hydride	140
Tantalum hydride	140.5
$FeCl_3 \cdot 6H_2O$	141
Potassium chloride	143.5
Sodium chloride	144.5
Oxide on titanium diboride (green)	144.5
Titanium monoxide (yellow)	151.5
Titanium diboride (CVD and pellet)	165.0
Graphite	173
Electrophoretic carbon (1.5 h, 300° C)	175.5
Polytetrafluoroethylene	180

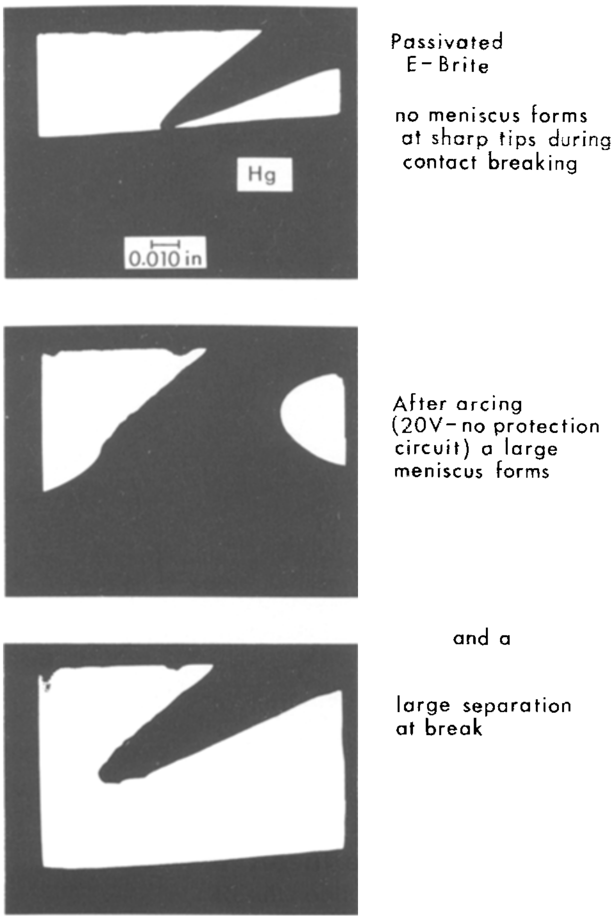

Figure 4 E-Brite (an alloy containing 0.005 max. C, 0.40 max. Si, 0.40 max. Mn, 25–27.5 Cr, 0.75–1.25 Mo, 0.0150 max. N, 0.5 max. Cu + Ni, balance Fe, w/o [7]) was passivated for 30 min in 70% nitric acid (6–15 v/o) aqueous solution at room temperature [8].

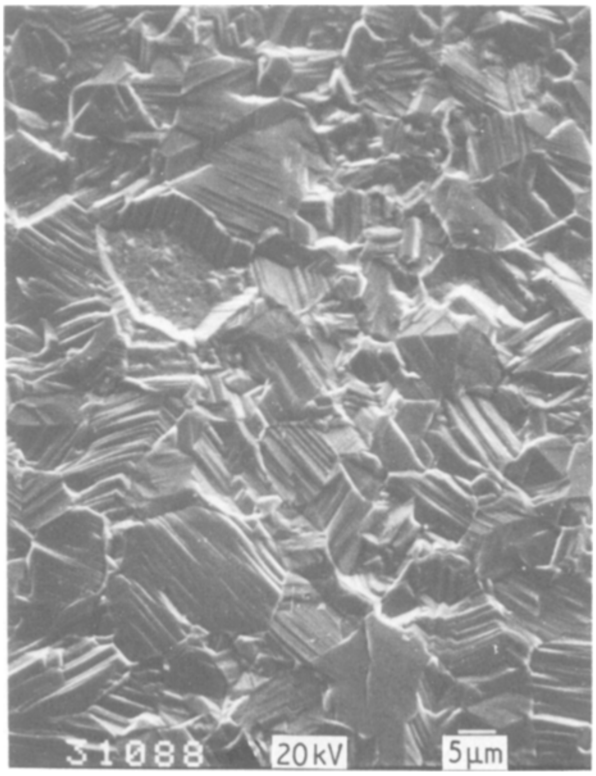

Figure 5 Scanning electron micrograph of a Kovar (29 Ni, 27 Co, 0.3 Mn, balance Fe, w/o) surface after etching in ferric chloride (42° Baume) aqueous solution at room temperature until a grey appearance was produced.

damage [5]. Our results show that arc protection circuits are essential if non-wetting and passivation are to be maintained.

Only two electrically conductive materials were found (graphite and electrophoretically deposited carbon after baking) which exhibited natural or intrinsic mercury repellent behaviour (analogous to water repellent). The menisci formed by these materials on retraction from mercury were not detectable at a magnification of 20×. Upon attempting to rest a mercury drop on these surfaces it was found that the slightest tilt of the sample or acceleration of the drop as it left the syringe resulted in the drop shooting across and off the surface. After many hours attempting to level the sample and to rest a drop on the surface with a success rate of less than 1%, we reconfigured for the measurement such that the flat sample was brought down into contact with the upper surface of a mercury drop confined in a depression in either a stainless steel or a graphite fixture. Contact angle measurements greater than 170° were then measured easily and were in agreement with those few which we were successful in obtaining from sessile drop measurements.

It was suggested that sharpening the tip of a sample rod would result in a much smaller mercury meniscus than that obtained on the flat end of a rod or wire [6]. We found that the meniscus height at break was negligibly small for a sharpened sample of an adherent but "non-wetting" material ($90° < \theta < 180°$). This was true also for the case where the mercury was retracted from the side of the rod as long as the tip was the last part in contact (Fig. 4). However, when the

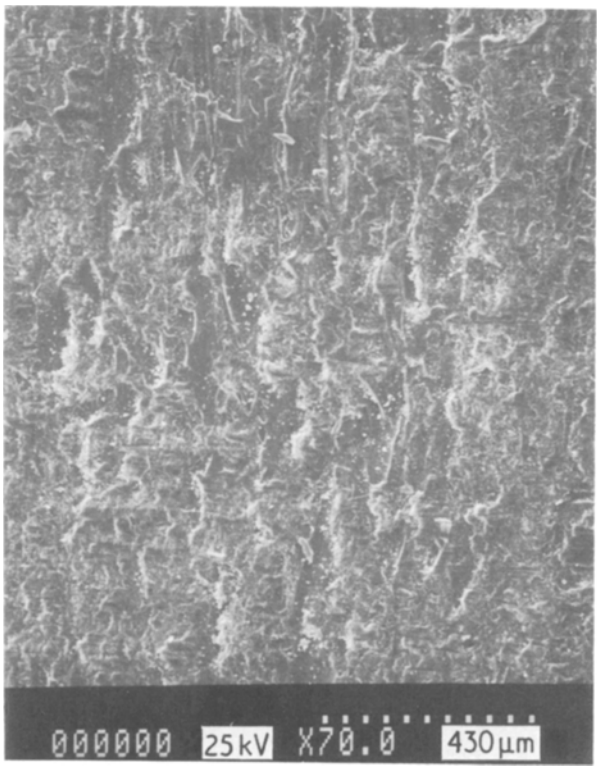

Figure 6 Scanning electron micrograph of a soda–lime glass surface after diamond scribing in a closely spaced cross-hatch pattern.

TABLE II Effect of surface roughening on mercury contact angle

Material	Contact angle		Roughening technique
	Polished	Rough	
Oxide on chromium	115.0	173.3	Ferric chloride etched kovar substrate, 100 nm sputtered chromium.
Soda-lime glass	124.5	173.7	Cross-hatch scribed.
Oxide on beryllium	136.3	173.0	Sputtered with 1000 eV hydrogen.
Oxide on 304 stainless steel	137.6	172.8	Oxalic acid etched.
Oxide on 304 stainless steel	137.6	172.8	Grit blasted.
Oxide on 308 stainless steel	141.7	170.8	Hydrochloric acid etched.
Oxide on kovar	144.9	172.5	Ferric chloride etched.
Titanium diboride	164.8	176.6	CVD on carbon felt.

material was rendered mercury wettable by arcing, a very large meniscus was observed.

It has been known for some time that certain types of surface roughening increase the effective contact angle for materials which have $\theta > 90°$ in the smooth condition. For example, the fabrics industries have increased the water repellence of garments by opening the weave (a form of surface roughness) [9–12] and a duck's back is water repellent because of the same type of geometrical structure of the feathers [11–13]. We obtained analogous repellence of mercury for materials which were adherent in the smooth condition by roughening using (a) a ferric chloride etch [14], (b) a hydrochloric acid etch [15], (c) an oxalic acid electrolytic etch [16], (d) cross-hatched closely spaced diamond scribing, (e) machined cross-hatching [17], (f) grit blasting [18] and (g) hydrogen ion bombardment [19]. These results are shown in Table II. The roughened surfaces have sharp features in common (Figs 5–9). Since $\theta > 90°$ for the materials in the smooth condition mercury does not wick into the valleys of the roughened surfaces (Fig. 10), and only small menisci are formed at the sharp surface features.

4. Conclusions

In a search for solid electrical conductor materials which do not adhere to mercury it was found that: (a) metals and metal oxides, carbides, borides, chlorides and hydrides adhered to mercury and formed mercury menisci of significant dimensions on separation; (b) arcing resulted in much longer menisci generally and corrosion in some cases; (c) sharpened electrical leads produced negligibly small menisci; (d) graphite and electrophoretically deposited and baked carbon exhibited natural mercury repellence; and (e) mercury repellence could be induced in otherwise adherent materials by several different means of surface roughening. Mercury repellent properties of rough substrates were replicated on deposited thin films. It should be noted that all of the results reported herein are for relatively short duration mercury–solid contacting and do not include time-dependent effects

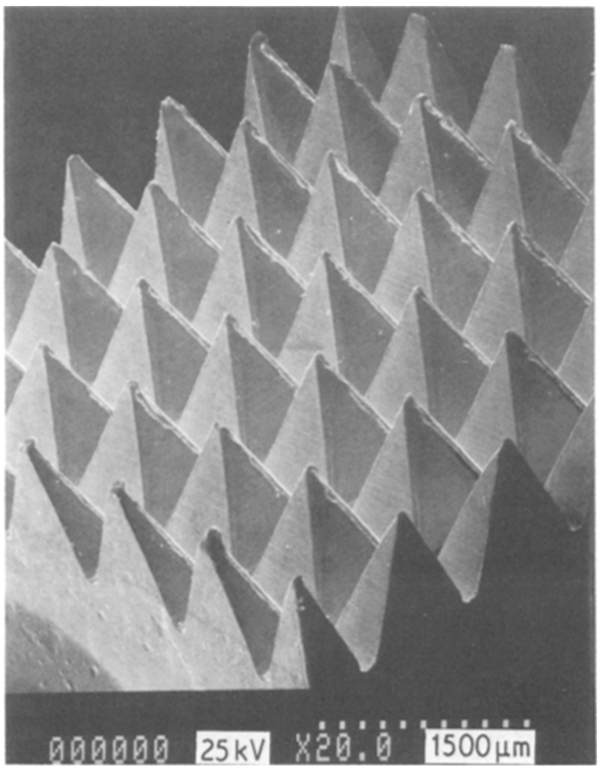

Figure 7 Scanning electron micrograph of a 304 stainless steel surface after micromachining [17].

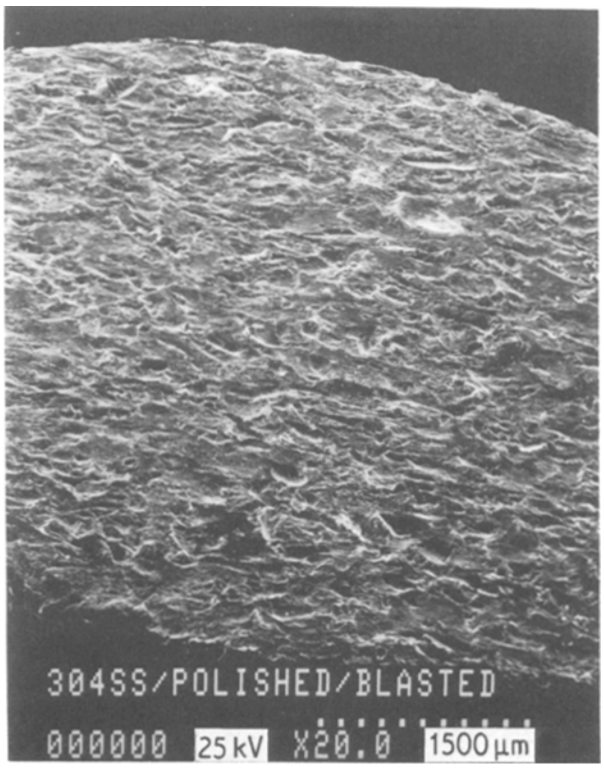

Figure 8 Scanning electron micrograph of a polished 304 stainless steel surface after grit-blasting with 2 mm silicon carbide particles until a uniform grey appearance was produced [18].

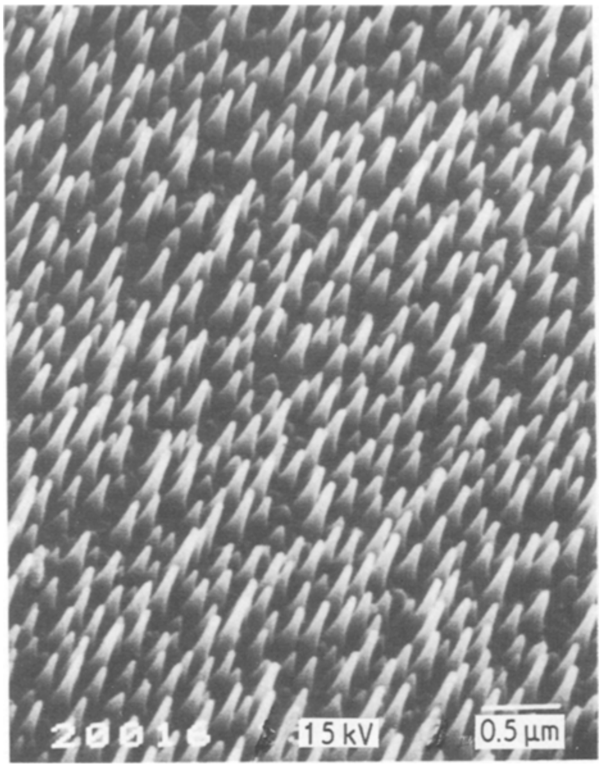

Figure 9 Scanning electron micrograph of a beryllium single crystal surface after sputtering with 1000 eV hydrogen ions (published by permission of J. K. G. Panitz, Sandia National Laboratories, Albuquerque, New Mexico).

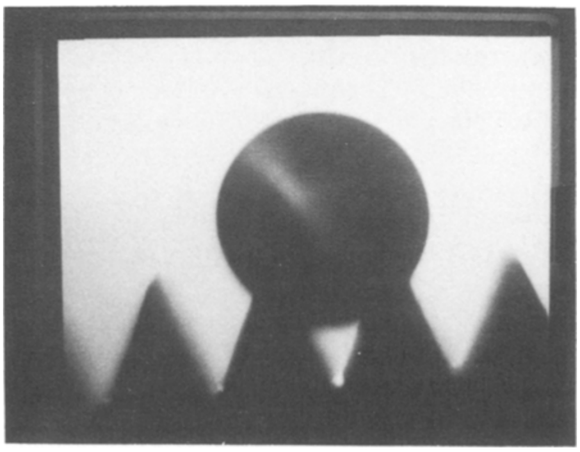

Figure 10 Backlighted mercury droplet resting on the micromachined 304 stainless steel surface shown in Fig. 7. Note that the mercury does not wick into the valleys.

which were attributed in earlier studies by Bonfield [20] to mercury slowly absorbing impurities from the solid.

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