Boundary lubrication effect of organic residue left on surface after evaporation of organic cleaning solvent

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Abstract

Although samples are visibly clean, organic deposits could have tremendous impacts on tribological measurements and interpretation of friction and wear behaviors. This paper discusses the boundary lubrication effects of invisible residues from organic solvents that have been widely used in tribological studies in ambient conditions. Stainless steel, soda lime glass, and copper substrates were cleaned using UV/ozone treatment or organic solvents such as alcohols where the solvent was allowed to evaporate from the surface. In ball-on-flat tribo-tests, all UV/ozone cleaned samples showed high friction and catastrophic wear immediately upon sliding due to the absence of lubricants at the sliding interface, while samples cleaned by organic solvent experienced low friction and minimal wear for hundreds of reciprocating cycles. Analyses of the surface by atomic force microscopy and vibrational spectroscopy indicated that the solvent cleaning deposits hydrocarbon residue on metal and oxide substrates. This residue is due to trace impurities with low vapor pressures inevitably present in the bulk liquid, regardless of solvent

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4 purity, which become concentrated upon vaporization of the high vapor pressure solvent. These
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6 results demonstrated that drying after cleaning with organic solvents is equivalent to a dip-
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8 coating of low vapor pressure organics onto the sample surface. This dip-coating effect can be
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10 avoided if surfaces are cleaned using UV/ozone or if the surface is immediately rinsed with DI
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12 water and blow-dried after cleaning with organic solvent. These results indicate that the friction
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14 coefficients of the samples with organic residues should not be interpreted with the shear
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16 strength model of friction.
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Introduction

Sample cleanliness is crucial for accurate measurements of friction and wear behaviors of sliding surfaces. Dry sliding between two surfaces that are in intimate contact can be affected by a very thin layer of lubricant. Self assembled monolayers (SAMs) have been shown to lubricate surfaces in atomic force microscopy (AFM) studies as well as decrease adhesion in microelectromechanical systems (MEMS) [1,2]. Many solid surfaces show a low friction coefficient near 0.2 and minimal wear with only a monolayer of adsorbed alcohol vapor [3,4]. This lubrication occurs not only at the nano-scale; it is also observed at the macro-scale where the surface roughness is several orders of magnitude larger than the size of adsorbed molecules [3]. Vapor can also be used to deliver a thin molecular coating to protect surfaces from wear [5–7].

Crucial to the proper function of these boundary lubrication methods is careful control of the chemical species on the surface. In the absence of any coating, pure metal surfaces could irreversibly adhere to one another and friction coefficients for these materials could be much higher than one [8–10]. Exposure to ambient air will form oxide layers on substrates with high surface energy [11–13]. It can also introduce a thin layer of organic contaminants adsorbed from the gas phase. These organic molecules can react to form adventitious carbonaceous deposits on surfaces in assistance of frictional heat or electricity, which can influence the tribological properties of the system [14–16].

This paper examines the effect of cleaning tribological surfaces with commonly-used organic solvents, with specific focus on the residue left after solvent evaporation. Soda lime glass (SLG), stainless steel (SS), and copper substrates were cleaned using two methods: (i)

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4 UV/ozone and (ii) rinsing with alcohol followed by evaporation or blow dry from the sample
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6 surface. The experimental results indicated that the residue film resulting from the evaporated
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8 liquid lubricates SLG, SS, and Cu surfaces with low friction and virtually no wear for a certain
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10 period which varies depending on the residue film thickness and sliding conditions. Since SLG,
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12 SS, and Cu have very different surface chemistry and physical properties, this effect is not a
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14 material specific phenomenon. Even if only a trace amount of residues is present in ultra-high
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16 purity solvent, the evaporation of solvent results in concentration of these residues on the
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18 substrate. Thus, the solvent cleaning and evaporation could be considered or equivalent to a dip-
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20 coating of low vapor pressure organic residues which inevitably exist in liquid solvents. Based
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22 on the findings from this study, the shear strength model of friction for *unlubricated* solids is
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24 revisited [17,18].
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33 Experimental

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35 Friction tests were conducted using a custom-built reciprocating ball-on-flat tribometer
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37 [19]. Substrate material was AISI 440C stainless steel (SS), oxygen-free high-conductivity
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39 (OFHC) copper (Cu), and soda lime slide glass (SLG). Commercially available 3 mm diameter
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41 440C stainless steel balls were used as a counter-surface for all copper and stainless steel
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43 substrate tests; 2.4 mm diameter borosilicate glass balls were used for SLG substrates. The
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45 tribometer was operated at a sliding speed of 4 mm/s with a 1N load for each test and slide tracks
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47 were roughly 2.5 mm long. All tests were conducted in a gas environment of dry nitrogen and
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49 were repeated for at least 5 times. The nominal Hertzian contact pressure for SS ball against SS
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51 substrate, SS ball against copper substrate, and glass balls against SLG substrate are calculated to
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53 be 642MPa, 524MPa, and 350MPa respectively. Previous vapor phase lubrication studies
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showed that SS, Cu, and SLG substrates do not get damaged mechanically as long as the surface is covered with one monolayer of alcohol molecules [3,12]. Thus, friction and wear tests at these contact conditions are sensitive to chemical conditions of the sliding interface.

All substrate samples were cleaned by rinsing with ethanol, followed by exposure to UV/ozone cleaning for at least 20 minutes. Tribotests investigating this surface were conducted immediately following UV exposure. For tests investigating the effect of cleaning with liquid solvent, the sample was taken from the UV/ozone chamber and then rinsed by the liquid in question, with liquid left on the sample to evaporate in air. Liquids investigated were ethanol, methanol, isopropanol, and decane, and each liquid had purity greater than 99%. After drying, these samples were tested using the tribometer.

Infrared spectroscopy analysis was carried out using a Thermo-Nicolet Nexus 670 system equipped with a MCT detector. Attenuated total reflection (ATR) tests were conducted for a liquid sample using a multi-bounce silicon crystal [20]. Polarization-modulation reflection-absorption infrared spectroscopy (PM-RAIRS) was used to analyze organic species remaining on metal surfaces; detailed description of the setup is available elsewhere [19]. For chemical analysis of organic species on SLG surfaces, vibrational sum frequency generation (SFG) spectroscopy was used [21]. Briefly, the SFG signal was generated at the substrate/air interface where two laser pulses – 532 nm visible pulses with 60° incident angle from an EKSPLA Nd:YAG laser and tunable IR pulses with 56° incident angle generated with an optical parameter generator and amplifier – were spatially and temporally overlapped. The SFG signal was collected in a reflection geometry and normalized with the input intensities of visible and IR pulses. The polarization of light was *s* for SFG signal, *s* for visible beam, and *p* for IR beam (*ssp*).

Topography of the wear tracks were analyzed with a Zygo NewView 7300 profilometer in ambient environment. The surface topography of samples with different cleaning methods were investigated by using atomic force microscopy (AFM) with a Digital Instrument MultiMode scanning probe microscope. Topographic images of the sample surface were collected with a contact-mode scanning. The AFM image size was $5\ \mu\text{m} \times 5\ \mu\text{m}$.

Results and Discussion

The lubrication of evaporated solvent residue was tested on glass, stainless steel, and copper. Figure 1 compares the friction behavior for stainless steel (SS), soda lime glass (SLG), and copper cleaned by either UV-ozone or by liquid ethanol. All tests were conducted in dry nitrogen. Figure 2 shows the surface profile of each material after friction tests. The severely worn surfaces with wear depth deeper than several microns (Figures 2a, 2c, and 2e) were observed for the samples cleaned with UV/ozone. When sliding was stopped before friction increased abruptly, the ethanol-cleaned surfaces showed only plastic deformation and no significant wear (Figures 2b, 2d, and 2f).

Figure 1: Friction coefficient for various substrates cleaned by UV/ozone or liquid ethanol. All tests conducted in dry nitrogen environment.

Figure 2: Optical profilometry images for SLG, SS, and Cu wear tracks. SLG is depicted in “a” (ozone cleaned) and “b” (ethanol cleaned); SS is depicted in “c” (ozone cleaned) and “d” (ethanol cleaned) and Cu is depicted in “e” (ozone cleaned) and “f” (ethanol cleaned). All scale bars are 100 μm and the color legend is to the right of each image. Polishing scratches for SS and Cu are horizontal.

Both friction and wear behaviors show that there is a drastic difference between the surface cleaned by UV-ozone and the surface cleaned by ethanol. All materials cleaned by UV-ozone experience wear and high friction immediately at the start of the tribotest. The value near

0.3 is typical of SLG substrate wear, which occurs through scratching/abrasion and creates piles of particulate debris, which is evident at the far edges of the optical profilometry image in Figure 2a. The friction value for SS is higher than 0.5 and the surface is severely damaged due to adhesive wear, as seen in Figure 2c. Similar behavior is seen for Cu in Figure 2e, with a friction coefficient higher than 0.6. The worn tracks from the UV-ozone cleaned surface measure several microns deep for each material.

These friction and wear patterns are in contrast to the negligible wear and low friction observed for the ethanol-cleaned samples. Friction for SS and SLG begins near 0.1 and slowly rises towards 0.2 as sliding continues, while friction for Cu is constant near 0.18 until wear occurs. Wear, or evidence of material removal by rubbing, is nearly imperceptible on the materials during the low friction period. The sliding track on SLG (Figure 2b) shows no height difference from the surrounding surface and is discernible mainly due to the minute pile-up of material at the periphery of the sliding track, whose height measures only tens of nanometers. The SS sliding track is virtually wearless (Figure 2d); only a slight depression due to plastic deformation in the bulk can be recognized. The Cu track (Figure 2f) is somewhat easier to see due to larger plastic deformation of the softer copper substrate.

The residual deposits from ethanol cleaning were further investigated by AFM. Figure 3 shows topographic images for a glass surface cleaned by liquid ethanol and then the same surfaces after cleaning with UV/ozone. The images from the ethanol-cleaned surface clearly show residual deposits distributed around the sample that measure up to 4 nm (Figure 3a). The glass surface becomes essentially featureless in the topographic image after cleaning with UV/ozone as seen in Figure 3b.

Figure 3: AFM topography image for cleaned glass surfaces: (a) Ethanol-cleaned SLG surface; (b) Ethanol-cleaned and then UV-ozone cleaned SLG surface. Brighter color represents a higher value and darker color represents a lower value. The size of the images is $5\ \mu\text{m} \times 5\ \mu\text{m}$.

The chemical nature of the organic material left behind by ethanol cleaning was investigated by PM-RAIRS and SFG. Figure 4 displays the spectral difference between liquid ethanol taken by ATR-IR and the deposit from evaporated liquid ethanol on copper taken with PM-RAIRS. Only the spectrum of the ethanol-cleaned copper substrate is shown here because copper gives better PM-RAIRS spectra due to its better IR reflectivity than SS and SLG, but the nature of remaining chemical species is expected to be the same for SS and SLG [22]. The evaporated ethanol spectrum shows a sharp peak near $2925\ \text{cm}^{-1}$ and another near $2850\ \text{cm}^{-1}$, typical of C-H stretching of CH_2 groups. Note that these peaks look very similar to the CH_2 asymmetric and symmetric stretch modes, respectively, of long-chain alkyl groups as seen in various SAMs and alkane molecules adsorbed on metal surfaces [3,23–25]. These alkyl stretching vibrations are different than those seen in liquid ethanol. The strongest peaks in liquid

ethanol occur at 2975 cm^{-1} and 2890 cm^{-1} , with a shoulder near 2930 cm^{-1} . These peaks represent the CH_3 asymmetric stretch (2975 cm^{-1}), the CH_2 Fermi resonance or CH_2 asymmetric stretch (2930 cm^{-1}), and the CH_3 symmetric stretch (2890 cm^{-1}) [26,27]. Absent from the evaporated liquid spectrum is the OH signal of alcohol centered near 3330 cm^{-1} , which is very strong and broad in the liquid spectrum. The absence of the OH stretching peak as well as the peak positions of the C-H stretching modes indicate that the residue on the copper surface is long-chain hydrocarbons in nature and lacks a hydroxyl group.

Figure 4: ATR-IR spectrum of liquid ethanol (red) on a Si crystal and PM-RAIRS spectrum of residue from ethanol after evaporation of the liquid (blue) on a Cu substrate.

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4 This nature was further investigated with SFG. Figure 5 compares the SFG spectra of
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7 SLG slides cleaned in various ways in different gas environments as well as the SFG spectra of
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10 liquid-air interface for ethanol and methanol. The liquid ethanol spectrum shows two peaks at
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12 2875 cm^{-1} and 2930 cm^{-1} . In contrast, both ethanol-cleaned and UV/ozone cleaned SLG surfaces
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14 shows three peaks at 2850 cm^{-1} , 2875 cm^{-1} , and 2930-2935 cm^{-1} . In SFG, the 2850 cm^{-1} peak is
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16 characteristic to hydrocarbons longer than the ethyl group [28]. Thus, its presence is an evidence
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18 for the presence of adventitious hydrocarbon contamination on the UV/ozone cleaned surface
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23 The SFG intensities of the hydrocarbon peaks are stronger for the ethanol-cleaned surface
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25 than the UV/ozone cleaned surface. In addition, there are some differences in spectral features
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27 compared to the adventitious hydrocarbon peaks on the UV/ozone cleaned surface. The
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29 asymmetric stretch peak is slightly shifted to 2935 cm^{-1} and the relative intensities of the
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31 symmetric stretch peaks (2850 cm^{-1} and 2875 cm^{-1}) are stronger than the asymmetric peak. Thus,
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33 the organic species on the ethanol-cleaned surface appear to be more abundant and different than
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35 those on the UV/ozone cleaned surface.
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Figure 5: SFG spectra with *ssp* polarization for (1) liquid ethanol in ambient air, (2) ethanol-cleaned soda-lime glass in ambient air, (3) UV/ozone cleaned soda-lime glass in ambient air, (4) ethanol-cleaned soda-lime glass in methanol vapor environment, (5) UV/ozone cleaned soda-lime glass in methanol vapor environment, and (6) liquid methanol.

In order to test how these surfaces cleaned with two different methods respond to the exposure to organic vapors, SFG analysis in methanol vapor was carried out. The liquid methanol spectrum has a unique sharp peak near 2830 cm^{-1} , along with a weaker peak near 2940 cm^{-1} in the *ssp* SFG spectrum (Figure 5). Since only methoxy group shows the peak at 2830 cm^{-1} [28], this peak is a good indicator that can be used to distinguish the presence of methanol molecules from other hydrocarbons. Upon exposure to the methanol vapor of the UV/ozone

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4 cleaned surface, the 2830 cm^{-1} and 2940 cm^{-1} peaks of the adsorbed methanol become dominant
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6 and much stronger than the adventitious hydrocarbon peaks. This indicates that the UV/ozone
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8 cleaned surface is *sufficiently clean* to allow adsorption of methanol molecules from the vapor
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10 phase. The relative intensities of two peaks of the adsorbed methanol are different from those of
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12 the liquid methanol. This must be due to the orientation difference of methanol molecules at the
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14 solid and liquid surfaces [28]. This result is consistent with the fact that the UV/ozone cleaned
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16 surfaces exhibit high friction in dry nitrogen and strong dependences on chemical composition of
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18 the surrounding gas environment [3,4,29].
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24 In the case of the ethanol-cleaned surface, the growth of 2830 cm^{-1} peak is also noticeable
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26 upon exposure to the methanol vapor, but not as prominent as the UV/ozone cleaned surface.
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28 Moreover, the asymmetric stretch peak is still centered at 2930 cm^{-1} , instead of 2940 cm^{-1} . This
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30 result implies that the methanol adsorption occurs, but its surface coverage is very small or
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32 limited since the surface is already covered with organic deposits from the ethanol solvent. Thus,
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34 the friction and wear behavior of the ethanol-cleaned surface would be dominant by the organic
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36 deposits from the solvent, rather than the molecules adsorbed from the gas phase.
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42 The low friction behavior that results from evaporated ethanol is also seen for other
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44 organic liquids. Figure 6 compares friction behaviors for SLG that was cleaned with UV/ozone
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46 versus different liquids. These liquids include an alkane, a branched alcohol (isopropanol which
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48 is another commonly used cleaning solvent) as well as the simplest alcohol (methanol). The
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50 liquid-cleaned surfaces exhibit low and stable friction near 0.1 or below for the duration of the
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52 experiment and the corresponding glass surface (not shown) shows no wear. Differences in
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54 friction coefficient may be due to different thickness or types of residue film [30].
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Figure 6: Friction coefficient for the resulting residue from different evaporated solvents compared to a UV/ozone cleaned surface. All data comes from SLG substrates and tests were conducted in dry N₂.

Figure 6 also includes results from a sample that was cleaned by liquid ethanol but then rinsed by DI water immediately after ethanol cleaning without allowing evaporation of ethanol. This replaces the organic solvent and residue on the surface with clean water. The water on the sample was then blown away from the testing area. Since water molecules have **stronger** interactions (for example, hydrogen bonding interactions) with the surface than organics [20], the strongly bound water appears to prevent or minimize the deposition of organic residue on the surface. This resulted in a high friction coefficient similar to the ozone-cleaned surface as well

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4 as significant ball and substrate wear, indicating that the glass surface is free from organic
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6 residual films.
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9 The organic liquids analyzed in Figures 1 to 6 are chemically different from one another,
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11 but all share two important characteristics: relatively low surface tension and high vapor
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13 pressure. These characteristics help to explain how the lubricating residue is accumulated at the
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15 surface. All liquids used were high purity (99% or higher, depending on chemical). No matter
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17 how small impurities are, they can be concentrated upon evaporation of the bulk liquid if the
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19 impurity has a vapor pressure lower than that of main solvent. In other words, the evaporation of
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21 the solvent ends up with concentrating impurities or additives with low vapor pressure which
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23 exist as a trace amount in the solvent. Thus, it will eventually result in a thin film or deposit on
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25 solid surfaces after drying. Unless the surface energy (or surface tension) of the solid is lower
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27 than that of these impurities, the evaporation process becomes equivalent to the ‘dip coating’
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29 process [31]. This contaminant can accumulate on the substrate surface as the bulk liquid
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31 evaporates, sometimes leaving an invisible film on the surface. This film is composed of the
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33 impurities in the liquid as well as any initial contaminant present on the surface.
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41 The value of the friction coefficient for different evaporated liquids appears to be
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43 different in Figures 1 and 6, but this cannot be attributed solely to chemical differences between
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45 the liquids. The drying liquid may not evenly distribute the resulting film across the substrate,
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47 leaving different coverages on the surface by a process known as the coffee-ring effect [32].
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49 Additionally, if the bulk of the film originates from impurities in the liquid, then the amount of
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51 liquid that evaporates will dictate the thickness of film formed. A larger amount of liquid over a
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53 smaller surface area will result in a thicker film that would give lubrication effects for a longer
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55 time. This can also affect the duration of lubrication; the friction coefficient for evaporated
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4 ethanol in Figure 1 slowly increases on SS and SLG surfaces, while the friction coefficient for
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6 the evaporated liquids in Figure 6 is relatively constant. The lubrication from the residue films
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8 in Figure 6 will eventually fail and the surface will begin to wear. The uncontrolled nature of
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10 residual film deposited on the surface makes quantification or precise chemical determination
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12 challenging, but Figures 4 and 5 indicate that the film is fundamentally different from the liquid
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14 alcohol.
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18 The value of the friction coefficient of 0.1 ~ 0.2 falls in the range that has been
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20 historically reported for the sliding of “*unlubricated*” smooth surfaces [17]. This friction
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22 coefficient value has been interpreted in a theoretical model considering the tensile strength and
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24 hardness of a material for asperity cold-welded junctions in metals. Starting with Bowden and
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26 Tabor’s theory for real contact area, Popov derived the shear strength necessary to break cold-
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28 welded junctions during the slide and arrived at a friction coefficient value of 0.16-0.2 for non-
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30 lubricated pairings of various solid materials [18]. However, it appears to be coincidental that
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32 this friction value matches those seen in Figures 1 and 6 for the samples cleaned with organic
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34 solvents. The analysis using tensile strength and hardness of the material relies on plastic
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36 deformation of the material and local cold-welding of asperities. This may be valid assumptions
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38 for most metals, but it cannot be applied to a brittle material like soda-lime glass [33]. The fact
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40 that both brittle (SLG) and tensile (SS and Cu) substrates have virtually the same friction
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42 coefficient (Figure 1) indicates that the lubrication due to the residue film is not specific to the
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44 material properties, but only requires a flat surface with an *invisible* film of organic residues.
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Conclusion

The tribological influence of cleaning by liquid solvents and their subsequent residue deposited by evaporation were investigated. Substrates on which alkane or alcohol solvents were allowed to evaporate showed good boundary lubrication and wear prevention compared to surfaces cleaned by UV/ozone. This lubrication was observed in a dry inert environment which otherwise should have caused high friction and considerable wear. The residue seems to originate from impurities in the liquid which accumulate on the surface as the higher vapor pressure solvent evaporates. This residual film can be negated by cleaning surfaces by UV/ozone or by rinsing a surface with DI water immediately following initial cleaning by organic liquid (before the organic liquid dries out). The theoretical model that attributes the friction coefficient of 0.1-0.2 for *unlubricated* solid surfaces to the shear strength of materials cannot be applied to the solid surfaces covered with *invisible* organic residues from cleaning solvents.

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