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Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Tribology Transactions

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/utrb20>

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Accepted author version posted online: 08 May 2013. Published online: 25 Jun 2013.

To cite this article: Tony Ying & Richard Gates (2013) Nanotribology Application in the Coining Industry (II)—Optimization of Lubricant Film Formation on Blanks, Tribology Transactions, 56:5, 749-758, DOI: [10.1080/10402004.2013.797530](https://doi.org/10.1080/10402004.2013.797530)

To link to this article: <http://dx.doi.org/10.1080/10402004.2013.797530>

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Nanotribology Application in the Coining Industry (II)—Optimization of Lubricant Film Formation on Blanks*

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A new method has been developed to lubricate metal coin blanks during the coin production process. The lubricant is formed on the metal surfaces as a monomolecular film during burnishing, which provides an exceptional combination of chemical and tribological environments needed to promote reaction. Laboratory-scale burnishing simulations combined with surface analysis indicated the composition and nature of the films formed. A comparison of reactions on metal surfaces with and without burnishing confirmed the importance of the tribochemical process to the successful lubrication of the blanks. Implementation of this lubrication procedure to production lines has improved the surface quality of the coins and tripled the die life, resulting in considerable cost savings.

KEY WORDS

Additives; Burnishing; Forming; Friction; FTIR; Lubrication; Nanotribology; Rust Inhibitor; Tribochemistry

INTRODUCTION

This article is part 2 of a three-part series describing the application of nanotribology to solving strike quality and die life issues in the minting of coins. The first article described the general minting process and the new chemistries that were utilized to improve production quality issues with new quarter and dollar coins (Ying, et al. (1)). The process changed from the previous conventional spray-lubricated system where a liquid stamping oil lubricant was applied to coin blanks during pressing to a more controlled application of monomolecular films based on the chemistry of the surface. The first article covered the more practical topic of what worked and how it affected the surface quality of the coins and the die life. This article addresses the analysis of the surfaces to determine what chemical reactions took place on the surfaces, what films were formed, and what nanotribological processes were important to successful coining with this method.

To achieve a longer die life and maintain a high coin surface quality, six requirements on top blank surfaces were postulated

over the course of this study. The required physical and chemical properties on a blank surface were as follows:

1. The metal surface must be free of thick oxide generated during the coin blank annealing process.
2. The protective lubricant layer must be self-aligned on the surface (reactive group on the surface, hydrocarbon group away from the surface). The functional group of the surface-protecting molecules must react with the metal surface to form strong bonds.
3. The molecules in the protective layer must be closely packed to impede corrosive constituents (e.g., oxygen, water) from passing through the film to get to the metal surface.
4. The top exposed layer of the protective film must be hydrophobic so that, after burnishing, the blanks can shed rinse water easily to avoid forming water stains (a cosmetic defect) on the blank surfaces.
5. The layer must provide a lubrication function during coining to reduce the friction on the die-blank interface and mitigate wear effects that might either lead to cosmetic damage to the coin or limit die life.
6. Only one layer of the molecules is allowed on the blank surface. Extra layers of chemicals can cause deleterious material to accumulate on die surfaces during coining. This buildup has a negative effect on coin production quality as well as die life.

The application of a lubricating film to coin blanks also has to fit within the constraints of existing coin handling and processing equipment in a production line, from creation and cleaning of the blanks through final stamping to create the finished coin. For the coining lubrication mechanism developed and described in these papers, the key reactions take place during burnishing of the blanks. Burnishing in the correct chemical environment provides the combination of chemical and nanotribological pathways to create an effective lubricating film, resulting in successful forming of the coins and long die lifetime.

*Certain commercial equipment, instruments, or materials are identified in this article to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.



Fig. 1—Blanks are mixed with stainless steel balls and pickling compounds in a burnishing machine (color figure available online).

In the production environment, burnishing equipment like the one shown in Fig. 1 is used to prepare the blank surfaces under a selected chemical environment. Coin blanks, stainless steel balls, and an aqueous blend of chemical compounds are mixed in a bowl. A rotor at the bottom of the bowl provides the mechanical agitation necessary to move the coin blanks. The motion of the mill balls (or blanks themselves) sliding on blanks with the aqueous solution in the bowl is a process generally referred to as *burnishing*. Depending on the production and equipment, each batch may vary from less than a hundred pounds to a few tons. It was not realistic to test different chemicals in such a large system, so to simulate the burnishing process a small-scale ball mill was used in the laboratory. The ball mill container was 100 mm in diameter and 150 mm in length. Two thirds of the mill space was filled with 3.2-mm stainless steel balls, a few blanks, and selected chemical compounds. A flat rectangular (75 mm \times 25 mm) piece of blank material was also included in the ball mill for postburnishing analysis by Fourier transform infrared spectroscopy (FTIR). The size and shape of the flat sample is optimized to cover the sampling area of the grazing angle FTIR measurement window utilized in the analysis. The speed of the ball mill was 60 rpm. During rotation of the ball mill, balls were continuously sliding on blank surfaces in the aqueous solution. After burnishing, the test specimens were analyzed by FTIR and weight change was measured using an analytical balance. The data were compared with the samples that were simply immersed in the same aqueous environment. The difference in the two cases was used to evaluate the tribochemical effect (burnishing) on surface chemical reactions. The knowledge obtained from the burnishing tests was used to optimize the formation of monomolecular films on blank surfaces in the laboratory.

Role of Burnishing on Surface Reaction Product Film Formation

Because the special tribochemical reactions obtained by burnishing are a key nanotribological component to the optimum film formation in minting coins, it is instructive to first discuss model reactions in simpler systems. In the early stages of this

work, fatty acids were studied. Even though these compounds were not used in the blank preparation process, the test data were useful in understanding the burnishing mechanism and what kinds of films could be formed on the metal surfaces of coin blanks.

As early as the 1960s, tribologists tried to apply multiple lubricant layers onto copper surfaces and measure the reaction between the lubricant and copper (Menter and Tabor (2); Yoshioka and Yamamoto (3)). In the 1960s, Low, et al. (4) used glass wool to wipe oleic acid onto copper plates and then measured the absorption spectrum at different times and temperatures. By analyzing the infrared spectrum, they concluded the following:

1. At room temperature, freshly absorbed oleic acid had a very strong peak at 1710 cm^{-1} . The peak was due to the presence of carbonyl (C=O). With time, the intensity of the peak gradually reduced; however, a new peak at 1585 cm^{-1} appeared and its intensity gradually increased. After 232 min, the intensities of the two peaks were almost equal. At 70°C , after 612 min, the intensity of the peak at 1585 cm^{-1} was much stronger than the one at 1710 cm^{-1} .
2. The disappearance of the peak at 1710 cm^{-1} and appearance of the peak at 1585 cm^{-1} illustrated that the applied oleic acid gradually reacted with the copper surface to form copper oleate. The double bond between carbon and oxygen disappeared to form bidentate copper oleate in which both oxygen atoms in the acid group reacted with the copper atoms on the surface.
3. When the temperature was further increased to higher than 100°C , the decomposition of oleic acid and copper oleate occurred.

These results indicated that physically adsorbed oleic acid reacted with the copper surface to form a fatty salt that could be detected by the change in the FTIR spectrum. When the peak at 1710 cm^{-1} shifted to 1585 cm^{-1} , the hydrogen atom in the acid group was replaced by the copper. A new reacted product, copper oleate, was formed.

Hu, et al. (5) added stearic acid in paraffin oil and applied rubbing conditions using a pin-on-disk wear tester. By using frictional sliding, a layer of bidentate copper stearate complex was formed on the wear track after only 16 min. The C=O peak shifted from 1710 to 1585 cm^{-1} , indicating that the stearic acid reacted with copper to form copper stearate.

After the 1970s, monolayer film application technologies were widely used in research and industry (Stoddart, et al. (6); Ando, et al. (7); Bhushan, et al. (8); Agabekov and Zhavnerko (9)). There were many ways to generate layers of lubricant on solid surfaces (Stocland (10); Ma and Liu (11); Treverton, et al. (12); Cruz, et al. (13)), but a particularly effective method was tribochemistry. Furey, et al. (14) found that monoesters were polymerized onto aluminum surfaces during pin-on-disk tests. As with Hu et al.'s (5) work, FTIR spectra indicated that the C=O peak shifted to lower frequency after rubbing.

In the present work, oleic acid adsorption tests on the copper surface were repeated with the modification that an emulsified version was used. Oleic acid (0.5 wt%) was emulsified in deionized (DI) water by a strong ultrasonic source. A 25 mm \times 75 mm \times 1.5 mm metal plate, made of the same material used

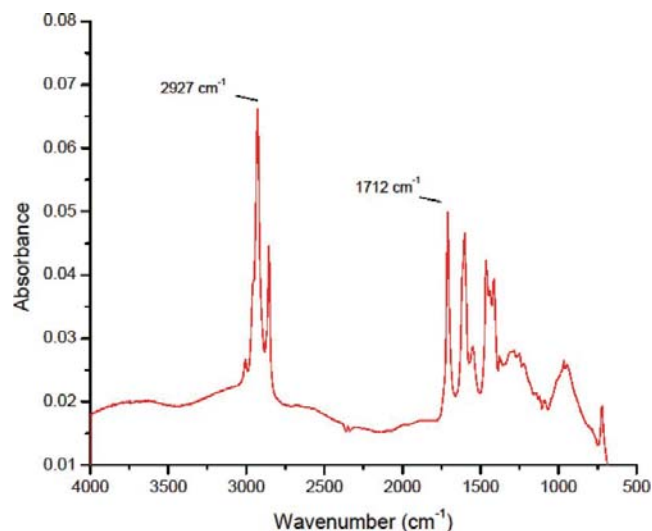


Fig. 2—Oleic acid physically adsorbed on copper surface after immersion in emulsion solution for 30 min (color figure available online).

in the one dollar coin, was polished by a series (240, 320, 600, 800, 1,200 grit) of SiC abrasive paper and water. The one dollar coin material is comprised of approximately 77% (by weight) copper, 12% zinc, 7% manganese, and 4% nickel. The polished plate was immersed in the oleic acid emulsion solution for 30 min (no ultrasonication). During the immersion period, the oleic acid continuously adsorbed on the surface and a film was formed. After rinsing with DI water and drying in air, the plate was analyzed with an FTIR spectrometer (Nicolet Magna-IR750). The absorption spectrum, as shown in Fig. 2, was obtained using an 85° grazing angle accessory that has the sensitivity to measure the chemical structure of very thin (even monomolecular) films on surfaces. The peak near 2928 cm^{-1} is due to the asymmetric C—H bond stretch vibration of CH_2 from the alkyl portion of the adsorbed oleic acid and its intensity is around 0.05 absorbance units (AU). The characteristic carbonyl (C=O) vibration was very clear and strong at 1712 cm^{-1} . The positions of the peaks exactly matched the peaks in Low, et al.'s (4) work indicating the presence of unaltered oleic acid molecules on the surface. All of the oleic acid molecules were merely physically adsorbed on the metal surface without any significant strong chemical reaction with the underlying metal.

The same emulsified oleic acid solution was poured into the ball mill. The plate was burnished with the solution for just one minute at room temperature. After burnishing, the plate was removed from the ball mill, rinsed with DI water, air dried, and analyzed with the FTIR. The spectrum is shown in Fig. 3. The C=O peak, originally observed at 1712 cm^{-1} , completely shifted to 1587 cm^{-1} . As analyzed in Low, et al.'s (4) work, the change indicated that the oleic acid had reacted with the copper surface to form copper oleate after only one minute of burnishing. The absence of any peak at 1712 cm^{-1} indicated that the film was entirely copper-bonded oleic acid and not physically adsorbed oleic acid. The reaction rate was much faster than in the stationary immersion case and also much faster than that observed by Low, et al.

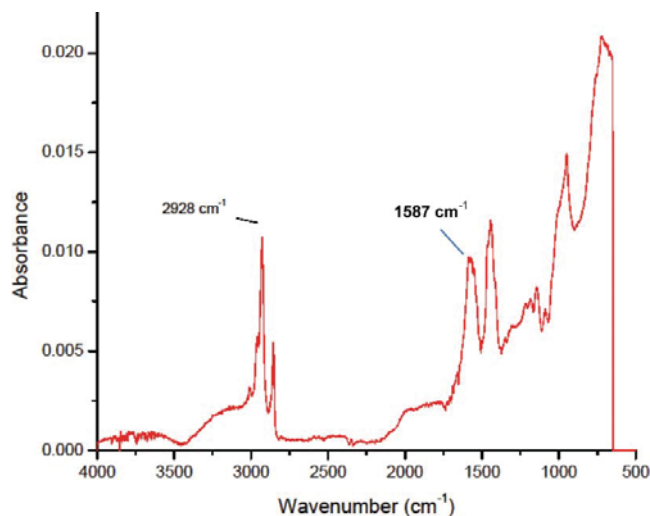


Fig. 3—Oleic acid reacted with copper surface to form copper oleate after burnishing for 1 min (color figure available online).

(4). The intensity of the CH_2 peak at 2928 cm^{-1} was only 0.01 AU, suggesting that the thickness of the layer was much thinner than that of the purely immersed sample. This was hypothesized to occur because the shear stress of the mechanical burnishing process probably also removed or prevented the physically adsorbed oleic acid molecules from building up on the surface. These reacted copper oleates were self-aligned on the surface with the acid group bonded to the metal and the hydrocarbon chain sticking out from the surface, imparting a hydrophobic character to the surface. The inference was that the burnished (chemically bonded to Cu) film was approximately one monolayer and the immersed (physically adsorbed) film was multilayer. If we assume the same areal molecular packing density on the surface, the immersed film was five times the thickness of the burnished film.

From these tests we confirmed that some observed chemical reaction rates on a solid surface could be accelerated by sliding movement. Thus, for coining, some useful chemicals could be purposely applied on the coin blank surfaces and form a strongly bound reaction product layer in a very short time using a burnishing process.

Role of Burnishing in Removal of Surface Films

To remove the residual stress generated during the rolling process, coin blanks are annealed, which creates an oxide layer on the outside surface. In the first article in this series (Ying, et al. (1)) the elemental composition of the coin blank surface was measured as a function of depth by glow discharge optical emission spectrometry. The depth profile is replotted in Fig. 4, showing a relatively thick (almost a micrometer) oxide film on the surface of the blank. The chemical proposed for use on coin blanks reacts with the metal in the blank, not the oxide, so before applying lubricant or antitarnish compounds on blank surfaces, this oxide layer must be completely removed.

The glow discharge optical emission spectrometry measurement indicated that the oxide layer was relatively thick at about 1 μm . An initial difficulty encountered was that on a normal

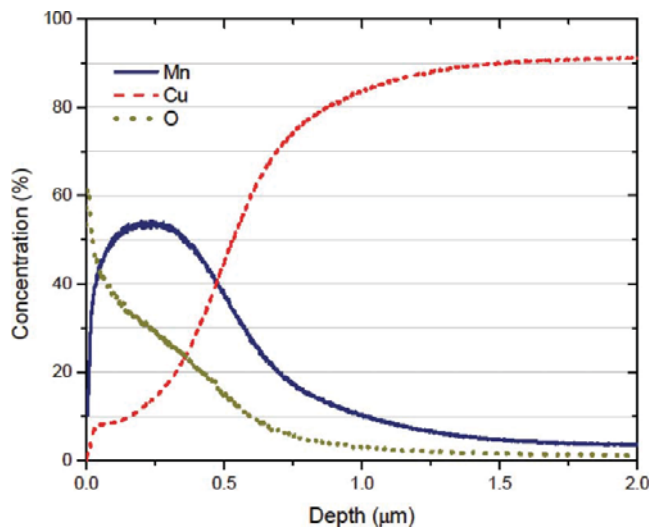


Fig. 4—Element concentration profile of an annealed one dollar blank surface (color figure available online).

production line the 1- μm -thick oxide layer could not be completely removed within an allowed processing time utilizing a purely chemical means, even with much higher pickling chemical concentrations. The burnishing process was studied as a means of removing the oxide more quickly.

Pickling is a general industrial term for a process that removes undesirable surface elements (e.g., contaminants, surface oxide). In this study, a commercial pickling compound based on citric acid (AC-67, Chem-Tech) was used for removing the oxide layer from the coin blanks on the production lines. The major ingredients in the compound were citric acid and surfactants. The metal oxide on a blank surface reacts with citric acid to form metal citrate salt, which dissolves in water and thus the surface oxide layer is slowly removed. Three annealed one dollar blanks were immersed in 200 mL of the pickling solution for 10 min. The solution contained 20% AC-67 and other surfactants. After 10 min at room temperature, the blanks were dried and weighed. The average weight loss was 0.6 mg.

The same process was repeated with three new annealed blanks but the ball mill apparatus was used instead. After 10 min of burnishing in the pickling solution at room temperature, the average weight loss was 4.6 mg. The average weight loss was almost an order of magnitude more than the immersed blanks for the same exposure time, attesting to the increased effectiveness of burnishing in removing the oxide layer. Though it is not completely understood whether the enhanced oxide film removal was due to an increase in the reaction rate between citric acid and metal surface from rubbing (tribochemistry) or a mechanical effect on the surface product removal (merely wear), the overall effect was substantial.

Some difficulties were encountered in attempting to export the pickling–burnishing technique to the full-scale production line operation. Because the exact conditions of the ball mill and the burnishing machine were different, the amount of added chemicals and burnishing times were varied. In the burnishing machine similar to that in Fig. 1, batches of 180 kg of blanks were

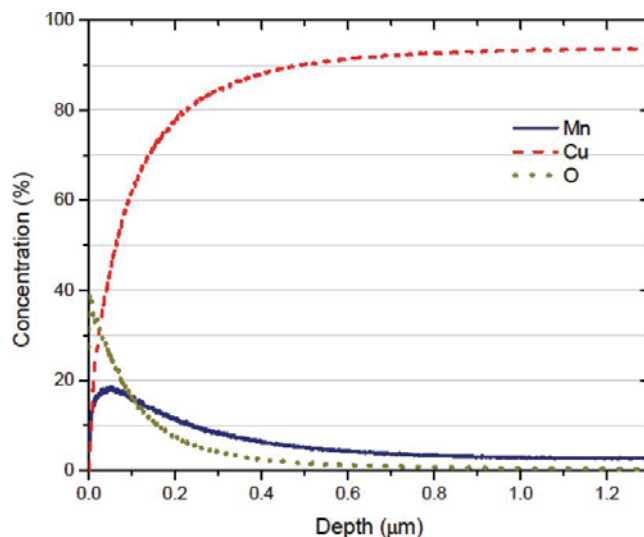


Fig. 5—With initial operation parameters, the oxides were not completely removed (color figure available online).

tested. The volume of pickling agent (AC-67) was varied between 0.5 to 3 L in different tests. The burnishing time was set from 150 to 600 s. Even after the longest burnishing times and largest amount of pickling chemical, the oxide layer could not be completely removed, as typified in the depth element profile shown in Fig. 5.

Rather than investigating the chemical aspects (e.g., concentration, reaction time) of the chemical reaction, the mechanical effect was considered. The flow pattern of the balls and blanks in the bowl was reviewed. Under the normal condition suggested by the manufacturer, the balls and the blanks had almost identical speed during rotation, which had the effect that there was little differential (sliding) movement between balls and blanks to accelerate oxide removal. The situation was therefore very similar to a blank simply being immersed in a pickling solution. To make the balls slide against the blank surfaces, the burnishing equipment was modified. Four 75-mm-high ribs were mounted on the rotor at the bottom of the bowl. When the rotor was spinning with these ribs, the mixtures were first pushed to the wall of the bowl by the centrifugal force and then climbed up along the wall and finally fell inside and formed spiral lines as shown in Fig. 1. With this flow pattern, the balls moved much faster than the blanks. This ensured rubbing of the coin blanks, which, in the presence of the acid, caused the oxide removal rate to increase significantly. Even with less burnishing time, the blanks were pickled completely to a fresh metal surface. Finally, 1 L of AC-67 was added into the bowl and the burnishing time was set at 240 s. The elemental composition as a function of depth of a blank burnished with this process is shown in Fig. 6 and demonstrated complete removal of the oxide film under these conditions.

From these tests we understood that the chemical reaction rates on a solid surface could be accelerated by the tribological environment provided during burnishing. In one case (the oleic acid example), reaction product films were formed, and in another (the oxide film example), sacrificial reaction product

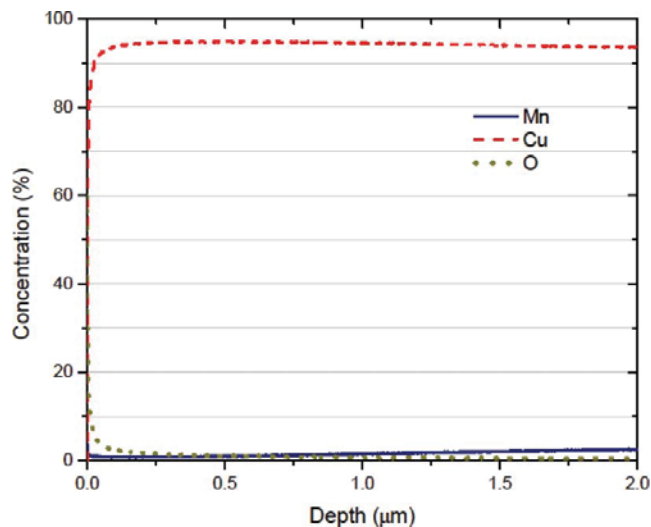


Fig. 6—Element concentration profile of a cleaned one dollar blank surface (color figure available online).

films were formed and subsequently removed. It should also be pointed out that for the oleic acid case, given the proper chemical environment, burnishing can cause both the formation of a strongly bonded monomolecular film and retardation/removal of weakly bonded (physically adsorbed) multilayer films that might otherwise be formed.

Balancing Monomolecular Reaction Product Film Growth and Multilayer Film Removal during a Burnishing Process

The previous test demonstrated the feasibility of using burnishing in a chemical environment to control the formation of a strongly (chemically) bonded monomolecular film without obtaining weakly bonded (physically adsorbed) multilayer films. The difficulty posed for applying this concept to the actual minting of coins is that specific performance criteria also need to be met. The film must lubricate the surface during the coin forming process. The final film must be hydrophobic and should not lead to tarnishing over reasonable lifetimes. This was accomplished using a combination of screening tests using a range of compounds and also applying some notions of what might be effective.

The first step was to decide what chemically reacted products should grow on the surface. As mentioned in the Introduction, the reaction layer must provide multiple functions. More than 30 chemicals, including fatty acids, amines, azoles, silicon oils, etc., were screened. None could meet all of the requirements. Some chemicals could not provide lubrication, some chemicals could not protect the blank surfaces from tarnish, some could not produce a hydrophobic film, and some could not be dissolved in water.

To obtain the multiple functions, one potential method was to combine two chemicals together. Based on this concept, dimethyl didecyl ammonium bicarbonate (DDBAC; commercially obtained as CarboShield 1000, Lonza Inc., Allendale, NJ; Bedard, et al. (15)) and benzotriazole (BTA, Fisher Chemicals, Pittsburg, PA) were tested.

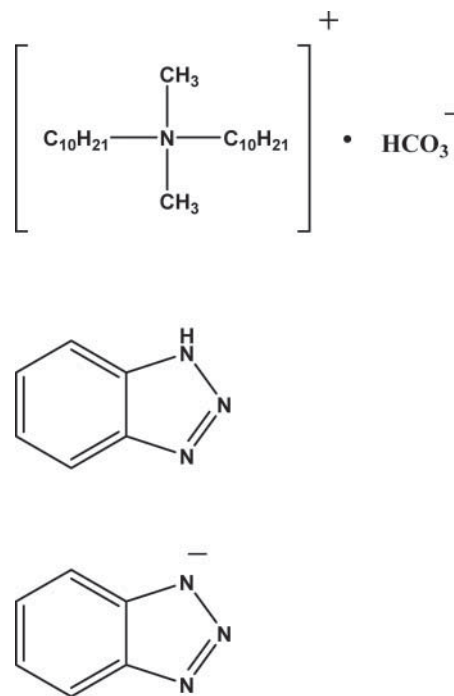


Fig. 7—Chemical structures of key components in the coinage process: (a) DDBAC; (b) benzotriazole; and (c) the negative ionic form of benzotriazole formed when the H is removed by reaction.

DDBAC is a liquid with a molecular structure as shown in Fig. 7a and an infrared (IR) spectrum (grazing angle on gold) as provided in Fig. 8. The most distinguishing features in the IR spectrum are the C–H stretch frequencies near 2900 cm^{-1} , the strongest of which are the C–H asymmetric stretching frequency of CH_2 at 2923 cm^{-1} and the C=O bond peak at 1628 cm^{-1} . BTA is a solid with the chemical structure as shown in Fig. 7b. The transmission FTIR spectrum of BTA mixed with KBr and pressed into a pellet is shown in Fig. 9. The main characteristic IR spectral

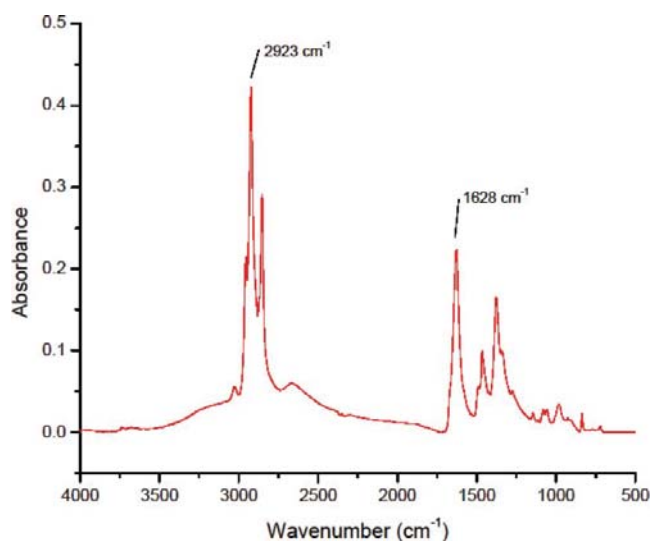


Fig. 8—FTIR spectrum of DDBAC (color figure available online).

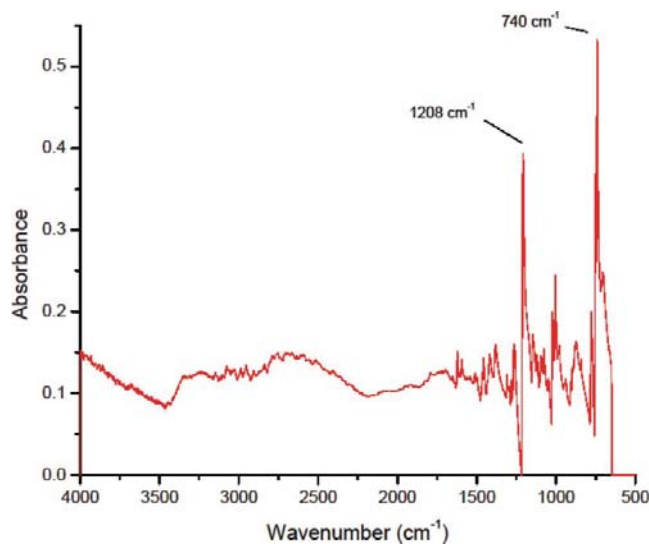


Fig. 9—FTIR spectrum of BTA on KBr pellet (color figure available online).

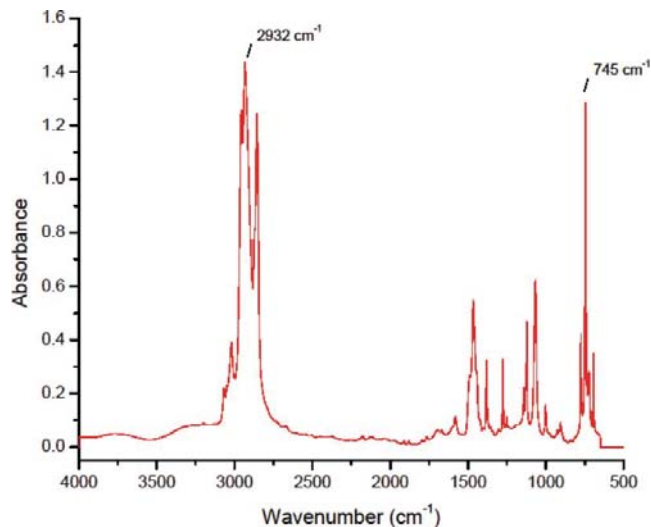


Fig. 10—FTIR spectrum of reacted product of DDBAC and BTA (color figure available online).

feature of BTA is the strong absorbance peak at 1208 cm^{-1} , which is attributed to C–H in-plane bending in the benzene ring (Billes, et al. (16)). This peak was considered by Nilsson, et al. (17) to be strongly dependent on the presence of N–H in the azole ring and the disappearance of that peak was attributed to hydrogen abstraction from the azole ring to form a negative BTA ion. A sample of BTA dissolved in DDBAC at room temperature produced the reaction product hypothesized in Fig. 7c with an FTIR spectrum as shown in Fig. 10. The wave numbers of the major IR absorbance peaks of these three chemicals are summarized in columns 2 through 4 of Table 1 along with some key structural assignments (column 1).

When BTA is mixed with DDBAC, many bubbles are observed, suggesting that carbon dioxide is formed as one of the

reaction products. This observation, coupled with the infrared spectral evidence, indicated that the carbonate had reacted with the hydrogen in the azole ring to form water and carbon dioxide. The C=O peak at 1628 cm^{-1} present in the original DDBAC was no longer present (Dragamoc, et al. (18)), suggesting the carbonate has participated in a reaction and has been altered. The peak at 1208 cm^{-1} of the BTA molecule also disappeared during the reaction, indicating that it, too, participated in the reaction. Because this peak relies on the existence of the N–H bond in the azole structure (Nilsson, et al. (17)), it was inferred that the N–H bond was absent and donated hydrogen to the reaction. The proposed reaction was that the hydrogen atom (from N–H) was abstracted from the azole ring of BTA and reacted with the carbonate of the DDBAC, creating carbon dioxide and water. This

TABLE 1—FTIR SPECTRA PEAKS OBSERVED FOR DIFFERENT SAMPLES

Structural Assignment	Peaks of DDBAC (cm^{-1})	Peaks of BTA (cm^{-1})	Peaks of Reacted Product of DDA-BTA (cm^{-1})	Peaks of Reacted Product of DDA-BTA Burnished on Coin Blank (cm^{-1})
Alkyl C–H	3026		3020	3020
Alkyl C–H	2955		2956	2956
Alkyl C–H	2923		2932	2928
Alkyl C–H	2853		2856	2855
C=O	1628	1621		
BTA bonded to Cu	1466	1466	1466	1619 (broad)
	1377	1381	1381	1467
		1266	1276	1387
Azole C–C with NH		1208		1270
C–H benzene ring		1146	1141	1143
			1122	
		1077	1066	
Triazole		1004	1001	993
H–C benzene ring		778	775	785
Benzene ring		740	745	749
C–C skeleton	722		722	722

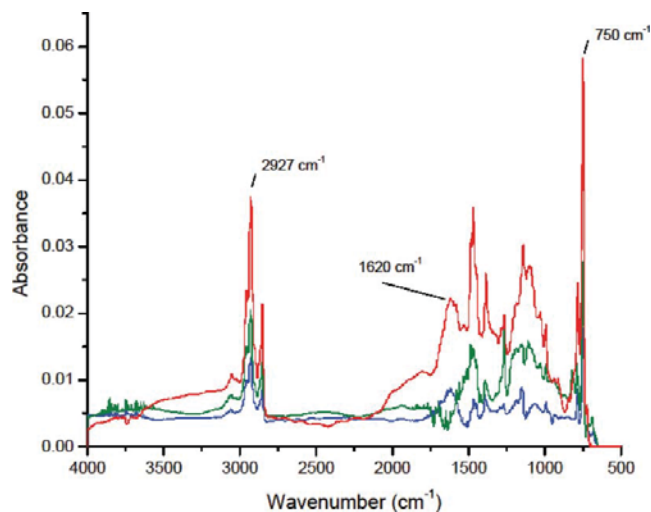


Fig. 11—FTIR spectra of DDBAC-BTA on blank surfaces generated with different conditions (color figure available online).

reaction created a BTA molecule with a negative charge and was balanced in aqueous solution by the positively charged dimethyl dodecyl ammonium (DDA) ion. As a result of the ionic character of the modified BTA, the solubility of the compound increased in water. The reacted product was diluted in water and called DDA-BTA.

A 25 mm × 75 mm × 1.5 mm flat test sample of the one dollar coin material was immersed in 200 mL of 5% DDA-BTA aqueous solution at room temperature for 10 min. The sample was then rinsed with DI water, dried, and measured with grazing angle FTIR. The presence of specific chemical structural markers in the FTIR spectrum confirmed that DDA-BTA molecules were merely physically adsorbed onto the coin metal surface. The FTIR spectrum is plotted in green in Fig. 11. Compared to the spectrum of the DDA-BTA reaction product in Fig. 10, most strong peaks of the reacted product appeared on the coin blank surfaces after the immersion process. It should be noted that there was no peak around 1620 cm⁻¹ in either spectrum. The structure of adsorbed molecules on the coin blank surface was the same as the reaction product present in the aqueous solution (DDA-BTA film cast on gold from an aqueous solution with the water evaporated as shown in Fig. 10).

The same flat test sample was burnished with the same 200 mL of 5% DDA-BTA solution in the ball mill for 10 min. After burnishing, the sample was removed from the ball mill, rinsed, and air dried. The coin blank sample was then measured by grazing angle FTIR, producing the red-colored spectrum shown in Fig. 11. The peak positions of the film from the burnished test sample are also listed in column 5 of Table 1. Compared to the peaks of the simple homogeneous reaction product of DDA-BTA (column 4) or the DDA-BTA simple metal immersion case, most peaks of reacted product also appeared on the blank surfaces after the burnish process. One significant difference was the presence of a new broad peak that appeared around 1620 cm⁻¹. This peak could not be from the original C=O bond, because it

was already reacted to form carbon dioxide, which bubbled away. It is necessary to discuss where this peak may be from.

In previous work, Nilsson, et al. (17) studied the FTIR spectra of a group of BTA complexes on copper and cuprous oxide-coated copper. The spectra of BTA on copper surfaces showed a peak at 1620 cm⁻¹ that was not present for an oxide-coated Cu surface, providing a clue that the peak observed for the burnished coin blank case was BTA bonded to copper. This is quite plausible considering that the coin metal is over 70% copper.

In the FTIR spectrum of the immersed sample without burnishing (green spectrum in Fig. 11), there was no peak at 1620 cm⁻¹, which is consistent with the spectrum of the homogeneous reaction product DDA-BTA and suggests that in the pure immersion case the DDA-BTA was weakly physically adsorbed. After burnishing (red spectrum), the broad peak around 1620 cm⁻¹ appeared on the surface, indicating that the molecule was (more strongly) chemically bonded to the surface. The tribological (burnishing) process resulted in a new chemically reacted product on the surface of the coin blank that had an infrared chemical signature of BTA bonded to copper. The presence of the CH₂ peaks in both cases also indicated that the alkyl chains of the DDA molecule were present and implied that the combination existed in the surface film, probably paired through ionic bonding.

The other difference between the two spectra (burnished vs. immersed) in Fig. 11 is the intensity of the peaks. The intensity of the CH₂ peak at 2928 cm⁻¹ for the immersed sample was 0.017, but for the burnished sample the intensity was doubled to 0.034, indicating a much greater abundance of CH₂-containing molecules on the surface. Assuming the same areal packing density of molecules on the surface and a single type of molecule (DDA-BTA), the burnished film appears to be about twice the thickness.

The coin blank material burnished with DDA-BTA did not exhibit any tarnishing and seemed to be somewhat hydrophobic; therefore, it was tested on the production line. After the blanks were stamped, the coins appeared to be well formed and did not easily form water spots, attesting to the ability of the compound to both lubricate the stamping process and provide a fairly hydrophobic surface coating. The coins were still well protected by the chemical layer and did not tarnish. During the continued coining process, however, a black contamination layer built up on the dies. The thickness of the layer increased very quickly such that after as little as 4–5 min, the die could not be used anymore without repolishing. As discussed in the previous article (Ying, et al. (1)), this black layer was an organic residue material transferred from the blanks to the dies during the coining process. Its existence was explained by reasoning that during the burnishing process, there was no process to control the thickness of the reacted film so that if there was more than one layer of the DDA-BTA on the blanks, the extra layers would be transferred to the die surface during coining. The transferred layers would gradually accumulate on the die surface, ultimately limiting the performance of the coining process. The die surface covered by the black deposited layer is called *dirt on die* by press operators and is an indication to stop the minting process to take corrective

action. The hypothesis that the lubricant film burnished onto the coin blank was too thick was supported by the observation of the peak intensities in Fig. 11.

Even though the DDA-BTA provided an excellent antitarish function, it was impractical to use on the high-speed coining production line due to the dirt on die contamination layer buildup on the dies. It was thought that the contamination problem on the die was due to the transfer and buildup of extra layers of the DDA-BTA generated during the burnishing process; therefore, the solution to this problem was to prevent multilayer films from initially forming on the coin blank surface so that only a monomolecular film remained. With the reacted metal-BTA bond, the molecules on the first layer were strongly bound and would not be transferred from the blank to the die. No transferred molecules would mean no accumulated contaminants on the die surfaces and, theoretically, the dirt on die issue would not arise. The basic lubrication concept was that a single strongly bonded monomolecular film would still provide sufficient lubrication to prevent cosmetic damage to the coin during the manufacturing process. The tribochemically induced (burnishing) process developed succeeded in creating a strongly bound monomolecular layer on the surface, but additional organic films also formed on top of this film, which introduced contamination problems. The new objective was to devise a way of removing the extra layers of film that were formed to avoid excess film transfer and contamination.

As discussed previously, depending on the properties, different chemicals can selectively remove materials from a surface. Thus, the second step of this process was to add a chemical compound to the burnishing mixture that would either remove the extra layers of the film generated on the surface during the same burnishing process or prevent the growth of the film beyond a monolayer.

In the oleic acid tests, there were two kinds of surface films. One was a weakly bonded, physical adsorbed, multilayer film. The other was a strongly bonded, chemically reacted film, thought to be a monolayer. During the burnishing process, the physical adsorbed film was removed and only the reacted film (Cu-oleate) was left on the surface. For the burnished DDA-BTA case, the first layer also reacted with copper to form a strongly bonded surface monolayer. Subsequent layers were only physically adsorbed on the surface. If a chemical could be found to remove the physically adsorbed layers but not affect the chemically bonded layer, it would provide the desired result of a strongly bound monomolecular film.

Screening tests were conducted using a variety of chemical compounds to see whether one could be found with sufficient solvency to remove the extra physically adsorbed layers without affecting the chemically bonded layer. Several variations and forms of chemicals such as alcohols, acids, ketones, and detergents were screened. Some, like citric acid, were too aggressive and removed all of the film on the surface. Some, like oleic acid, were too passive and either failed to remove the physically adsorbed films or actually helped grow additional films on the surface. Ultimately, a candidate compound was found that removed the physically adsorbed films but left the chemically bonded layer intact. This compound was termed *extra layer remover*, or ELR (the chemical

name is not disclosed at the manufacturer's request). The ELR was added into the DDA-BTA solution to burnish the test samples in the ball mill for 10 min.

After burnishing, the residual DDA-BTA on the test sample was measured by FTIR. The spectrum is plotted in blue in Fig. 11. The characteristic peaks of both the alkyl CH_2 of DDBAC and copper-bonded BTA were present, as in the spectrum burnished without the ELR (plotted in red), but the intensities of all peaks were significantly reduced. By comparing the intensities of the two spectra, it was estimated that the film thickness for the case of the test sample burnished with the ELR would be much lower. The intensity was also lower than that of the purely immersed sample, suggesting that the immersed sample may have been a multilayer film. No FTIR peaks characteristic of the ELR compound itself were left on the surface, indicating that the ELR functioned as a detergent to remove the extra film layers and was rinsed away completely.

The spectra illustrate that in the presence of ELR, the DDA-BTA layer grew on the surface by the burnishing process; however, extra film layers were not formed. Conceptually, this new process controlled the film growth and ideally only left a monomolecular reacted DDA-BTA-copper complex layer on the blank surfaces.

To obtain an estimate of the absolute film thickness on the coin blank surface, the intensity of the FTIR spectrum on a coin blank was compared with one of known thickness. Previously, Gates, et al. (19) demonstrated the ability to measure the thickness of a complex hydrocarbon film on a highly reflective (hard disk) surface using grazing angle FTIR. The model compound used, a multiply alkylated cyclopentane (MAC), was measured at film thicknesses from about 1 to 10 nm using the peak height of the CH_2 asymmetric stretch frequency. The key to calibrating the thickness of that compound relied on developing a special freeze-evaporation process for uniformly applying a known amount of MAC molecules to a surface in a dilute solution, freezing the solution and evaporating the solvent so that the MAC molecules ended up as a thin film on the surface. Uniformity of the film was confirmed using X-ray photoelectron spectroscopy and found to be better than 5% over a large (28 mm diameter) sample surface spot size. Grazing angle FTIR spectra that included the CH_2 asymmetric stretch region were quantified using peak height. Correlating the peak height against the deposited film thickness for a series of different concentrations of MAC in solvent resulted in a calibration curve of about 400 nm per absorbance unit of MAC film. Because the IR spectrum peak near 2932 cm^{-1} is specific to CH_2 , one can estimate a CH_2 contribution to film thickness from the MAC and use that value to roughly estimate an approximate film thickness for compounds containing CH_2 by factoring in the relative percentage of CH_2 in that compound to that in MAC. In the case of MAC versus DDBAC this is not necessary because they both contain the same concentration of CH_2 bonds per molecule. MAC contains 53 CH_2 bonds out of a total of 65 carbons per molecule (82%). DDBAC contains 18 CH_2 units out of a total of 22 carbons per molecule (also 82%). This suggests that a DDBAC film analyzed by the same grazing angle FTIR procedure with a CH_2 peak height of 0.01 absorbance units should be about 4 nm thick.

If the BTA portion also contributes to a physical dimensions of the film (but not the CH₂ peak in the spectrum) then the extra nine atoms (as a bonding pair with the DDBAC) would suggest that the film is actually slightly thicker. Because the extra nine atoms are in a more compact form (aromatic ring and azole ring) than a linear alkyl chain they would be expected to contribute less to the absolute thickness (perhaps only 25% more) such that the total experimentally measured film thickness is roughly estimated at 5 nm. This compares favorably with what one would expect for the thickness of an idealized continuous monolayer of DDA-BTA, densely packed on a perfectly flat surface (about 2 nm). This model film estimate was based on carbon-carbon bond lengths and assuming that the C10 alkyl chains are oriented vertically from the surface. Note that this model estimate assumes a perfectly flat idealized surface, whereas with a coin blank the surface is a real engineered surface with roughness. As a result, the film formed from the burnished DDA-BTA in the presence of the ELR as a monomolecular layer film.

The same thickness estimation logic can be applied to previous experiments conducted with oleic acid on copper (Figs. 2 and 3). Oleic acid has 18 carbons, of which only 14 contribute to the CH₂ asymmetric stretch (about 78%). This suggests that the copper oleate burnished film in Fig. 3 (0.01 AU) was also approximately 4 nm thick. Again, this is quite close to the 2 nm estimated for an ideal oleic acid monolayer, so the hypothesis of monolayer films for these real-world samples is fairly reasonable. The designation of the purely immersed oleic acid film in Fig. 2 (0.05 AU = 20 nm thick) as a multilayer physically adsorbed film is also reasonable.

Further Improvement of Molecular Structure of DDA-BTA

Though the monomolecular DDA-BTA film provided an excellent antitarnish function for the coin materials (from the BTA portion of the molecule), the overall performance with regard to lubrication and hydrophobicity were less than optimal because of the rather short alkyl chains on the original DDBAC. Each of the two long chains in the DDBAC have only 10 carbon atoms. From a lubrication potential perspective, this alkyl chain length could be improved by utilizing longer chain length alkyl compounds. It was also noted that the latest version (DDA-BTA + ELR) did not generate a completely hydrophobic surface. After water rinsing the blanks in the burnishing machine, water did not bead up very well on the residual DDA-BTA film and subsequently caused some water stains on the blanks after drying.

In an attempt to improve both the lubrication and hydrophobic performance of the film, a new compound was obtained in which the two decyl chains of the DDBAC were replaced by longer octadecyl groups. The new molecule was reacted with BTA as before to form a new chemical molecule—dimethyl dioctadecyl ammonium benzotriazole, more simply referred to as BTX. A BTX solution mixed with ELR was used in the ball mill to burnish the blank material samples. After 10 min of burnishing, a monomolecular layer had formed. The FTIR spectrum of the layer is shown in Fig. 12. Because the molecules have more CH₂ groups in the chain, the peak at 2928 cm⁻¹ is stronger relative to the benzene peak at 748 cm⁻¹ (compared

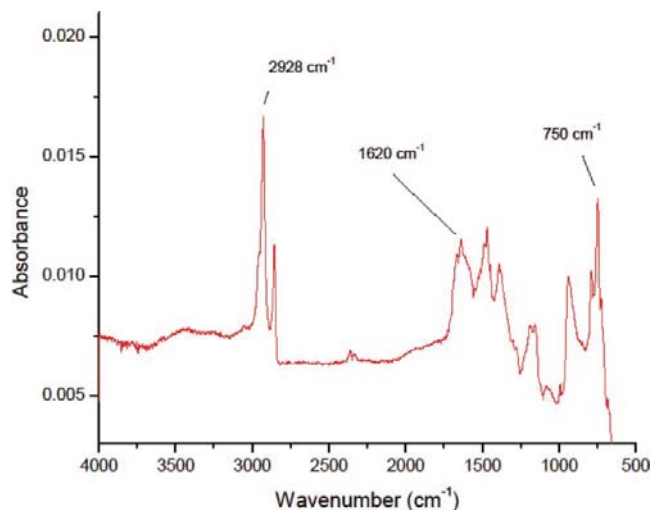


Fig. 12—FTIR spectrum of BTX film reacted on copper after burnishing (color figure available online).

to the C10 version shown in Fig. 11) The intensity of the CH₂ peak is about 0.011, again consistent with the higher percentage CH₂ contribution expected for the new longer chain molecule. The longer hydrocarbon chains on the surface contributed to the improved lubrication and greater hydrophobicity of the final film. The presence of the broad IR peak at 1620 cm⁻¹ is again characteristic of bonding between the BTA portion of the BTX compound and the copper surface.

Because the new BTX compound exhibited improved properties, it was implemented on a massive blank preparation line. Tons of blanks burnished with the new solution were sent to press for striking with the conventional stamping oil sprayer turned off. After the stamping of hundreds of thousands of coin blanks, no dirt on die contamination was observed on the die surfaces. In addition, inspection of the coins revealed no water spotting issues, no tarnishing, and high-quality, shiny surfaces. The quality of the process was so improved that stamping was able to be continued well beyond the usual lifetime of a typical die (about 140,000 strikes), with die lives using the new experimental lubrication process reaching 400,000 strikes.

CONCLUSIONS

A new lubrication process has been developed to allow minting of copper-containing coins for the U.S. Mint. From a practical standpoint, the overall effect has been to allow high-surface-quality coins to be made with favorable cosmetic qualities (low tarnish, no water spotting) with a substantial improvement (tripling) of die life. This has resulted in a cost savings to the U.S. Government of millions of dollars annually. From a scientific and technical standpoint, a near-monomolecular film lubrication method was developed based on an understanding of nanotribology, surface chemistry, and the unique potential for tribochemistry to aid in creating optimal surface films. Using a combination of bench-scale tests and highly sensitive analytical techniques for detecting the chemical structure of the surface films, a model has been proposed for how the film

is formed and behaves. This article explored the chemical and tribological processes important to the development of the new coin stamping lubrication process developed using the concept of monomolecular film lubrication. The successful application was based on the following essential processes and understandings:

1. An aqueous solution was formulated consisting of a mixture of precursor compounds designed to create a protective lubricating film on coin blank surfaces. Three key components were utilized: (i) a long alkyl chain portion that imparts lubricity and hydrophobicity to the resulting film, (ii) a benzotriazole portion that provides strong bonding to metal surfaces, and (iii) an undisclosed polar compound that acts like a detergent to prevent the formation of a multilayer buildup on the surface film that can lead to contamination of the repetitive striking portion of the tribological couple (i.e., the die).
2. Tribochemistry, provided through burnishing, is an essential component of the new minting process and is used in two ways. First, burnishing in the presence of an organic acid allows complete removal of oxide films left over from the coin blank annealing process in reasonable times. The resulting fresh copper surfaces are required for subsequent reaction steps. Second, burnishing is required in the presence of an optimized chemical compound (BTX) to induce the strong chemical bond between the benzotriazole moiety and the copper surface of the coin blank material. The result is a strongly bound monomolecular film with the desired lubricity, hydrophobicity, and antitarnish capabilities.
3. The presence of an undisclosed polar compound, ELR, is required during the burnishing step to prevent the formation of extra layers in the film and limit the film thickness to near-monomolecular dimensions.

The new monomolecular lubrication process has been successfully implemented on all production lines for nickels, dimes, quarters, and one dollar coins in the U.S. Mints in Philadelphia and Denver since 2010. To date billions of coins have been minted using this technique.

In the third article in this series, a thermodynamics model will be used to explain why the sliding environment of tribochemistry increases the chemical reaction rate on solid surfaces.

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