

PHOSPHONIC ACID A ZERO-ENERGY APPROACH TO TEFLON REPLACEMENT

Tom Appicella, Daphne Ezer, Brianna Fram, Dominique Ingato, Sarah Karinja, Marina Mainescu, Vincent Ning, Lucas Pratt, Alec Story, Sally Wang, Olivia Waring

Advisor: Michael Avaltroni
Assistant: Jeremy Tang

ABSTRACT

Octadecylphosphonic Acid (ODPA) is a hydrophobic substance that may be applied to any oxide surface – such as a metal or glass - to create an organic, hydrophobic non-stick coating similar to that of Teflon (Polytetrafluoroethylene). However, ODPAs covalently bond to the surface of oxides rather than physically sticking to a surface as Teflon does. As a result, ODPAs suffer none of the drawbacks of Teflon, including erosion or chipping of the surface (as in non-stick cookware), “creep” of the Teflon coating along a surface, and the carcinogenic qualities of the fluorinated Teflon molecule. Our goal was to create a method of applying this coating for production outside a laboratory, with a particular focus on low- to zero-energy methods to further entice industry. We found that by using a Meyer rod to apply ODPAs and allowing it to cure in a greenhouse on top of aluminum or galvanized steel, we could create coatings comparable to traditional, energy-intensive methods.

INTRODUCTION

The Need for a Teflon Replacement

Polytetrafluoroethylene (PTFE), commonly known as Teflon, is a synthetic compound widely used in both household and industrial environments. Because of its low coefficient of friction and high melting point, it is useful in a variety of applications, ranging from industrial lubricants and biochemical sieves to nonstick cookware and waterproof textiles. In addition, PTFE is highly inflexible and reacts with very few metals due to the strength of the carbon-fluorine polar bonds and the non-polar carbon-carbon bonds.

However, the perfluorooctanoic acid (PFOA) used to manufacture PTFE has been identified by the EPA as a potential carcinogen, which poses health risks because of PTFE's common role in cookware and orthopedic transplants. PTFE also contains high amounts of fluoride, a toxic and possibly carcinogenic chemical in humans. Finally, because PTFE is only physically bonded to the surfaces it is applied to, it flakes off easily [1].

ODPA and Oxide Surface Chemistry

Many different surfaces, such as titanium's, spontaneously form a protective oxide layer when exposed to atmospheric oxygen. Like most metals, titanium's oxide layer takes two forms: μ -oxo groups, where the oxygens are single-bonded to the surface in two separate locations, thus making them largely unreactive, and hydroxyl (-OH) groups where oxygens are only single-

bonded to the surface in one spot, making them much more reactive than the μ -oxo groups (Figure 1). Together, both types of groups form a protective, self-healing oxide surface that makes the original material largely inert: the surface prevents external forces or molecules from reaching and reacting with the underlying metal or glass, which is an oxide all the way through. Despite this unreactivity, however, there are some useful molecules that can react with the “inert” oxide layer to give comprehensive coverage of the surface. Such molecules have two end groups: the group labeled “R” attaches itself to the oxide layer, while the $-R'$ group performs a desired function, such as repelling water [2]. One such molecule is phosphonic acid.

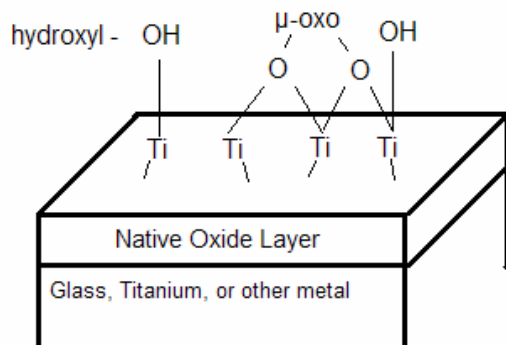


Figure 1. Oxide Surface

Phosphonic acid covalently bonds to the oxide coating, or performs a “controlled corrosion” on the titanium (or other metal). Phosphonic acid is derived from phosphonate, a compound comprised of a phosphorus atom that is double bonded to an oxygen atom, single bonded to two other oxygen atoms, and single bonded to an $-R$ group (Figure 3). The two single bonded oxygens are attached to other variable groups, R' and R'' . In phosphonic acids, both the $-R'$ and $-R''$ groups are hydrogens, that is, the phosphorus is attached to two hydroxyl groups [3]. The phosphonic acid used in our experiment, ODPa, has an eighteen carbon long alkyl chain as the $-R$ group; this highly non-polar chain increases the hydrophobicity of the resulting surface. Two advantages to using phosphonic acids are their stability under harsh conditions and their low toxicity in comparison to substitute substances such as PTFE. Phosphonic acids are very common in the biological world and thus relatively harmless [4].

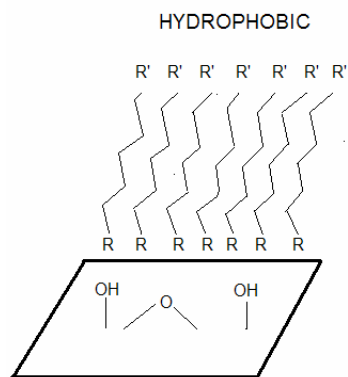


Figure 2. Self-Assembled Monolayer

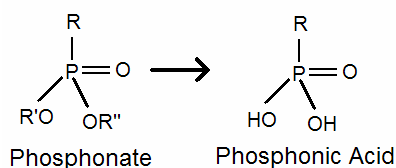


Figure 3. Phosphonates and Phosphonic Acid

When phosphonic acids covalently bond to the oxide surface, they form a self-assembled monolayer or SAM (Figure 2). This is a thin layer of a substance, less than 10 nm thick, which assembles itself spontaneously on the surface of a material [5]. In the case of phosphonic acids, the molecules bond covalently to the surface while forces such as hydrogen bonding between the oxygen and hydrogen atoms and Van der Waals attractions between the different phosphonic acid molecules stabilize the SAM [4]. It is this extensive bonding that makes phosphonic acids a favorable alternative to substances like Teflon; phosphonic acids bond chemically to the surface and these attachments are reinforced by intermolecular bonding. Teflon bonds physically through weak electrostatic forces that are easily disrupted by external forces [1]. The bonds that attach phosphonic acids to the surface are far stronger and thus longer-lasting.

In general, the reactions that bond phosphonic acids to the surface are simple: two separate reactions may take place, depending on whether there is a hydroxyl or μ -oxo group involved. If a hydroxyl group is involved, the phosphonic acid donates a hydrogen to the hydroxyl, thereby creating a surface-bound water molecule with a positive charge. The oxygen of the hydroxyl group is left with a negative charge. Bonding occurs when the water is removed. This is a simple dehydration reaction, and after the water is removed, the positive hole in the surface and the negative oxygen of the phosphonic acid form a covalent bond (Figure 4).

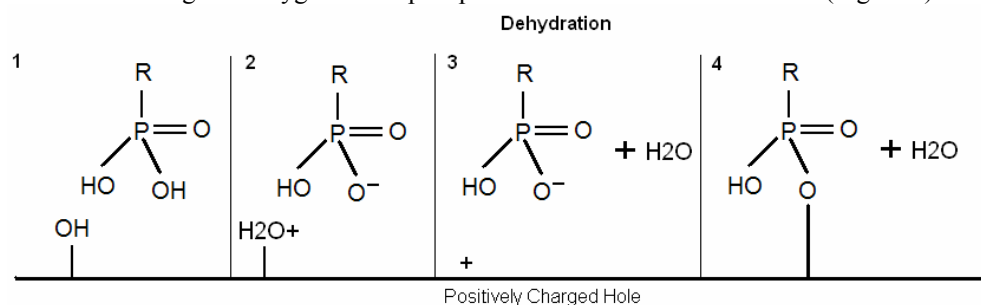


Figure 4. Dehydration reaction involving hydroxyl group

When a μ -oxo group is involved, the process changes. The phosphonic acid donates a hydrogen to the μ -oxo group, breaking one of the bonds attaching the oxygen to the surface. This leaves a new hydroxyl group and an "electron vacuum," while the oxygen on the phosphonic acid is left with a negative charge. This oxygen is attracted to the vacuum and creates a covalent bond, leaving the acid attached to the surface and a newly formed hydroxyl group (Figure 5).

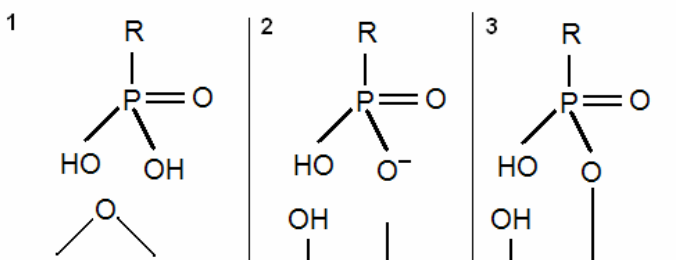


Figure 5. Dehydration reaction involving μ -oxo group

A third case sometimes occurs when a molecule of phosphonic acid that has already bonded covalently to a hydroxyl group on the oxide surface gives up another hydrogen. Phosphonic acids are diprotic and thus can give up two protons. Once the acid bonds to the surface by the hydroxyl group mechanism, it may form another covalent bond by the μ -oxo group mechanism explained. In other words, once the dehydration reaction has occurred, the second -OH group of the phosphonic acid can donate its hydrogen to a μ -oxo group, thereby resulting in a phosphonic acid that is doubly attached to the surface [4]. This also results in a new hydroxyl group, which allows another phosphonic acid to bond, resulting in more complete coverage of the surface.

These reactions are simple and easy to speed with heat, but even so they take a long time to go to completion, as the dehydration reaction is slow. In order to make phosphonic acids viable substitutes for Teflon, a fast and efficient method of applying and bonding the acids to the surface must be devised.

Coating the Surface

Our experimental procedure was divided into two distinct subsections. First, we physically applied a consistent amount of octadecylphosphonic acid to each glass slide before facilitating the chemical reaction that permanently bonded the ODPa to the oxide surface. While finding an economically viable way to execute the latter task was the primary objective of this investigation, physical application methods also played a key role in bonding. We chose to examine the relative merits of two application techniques: Tethering by Aggregation and Growth and Meyer Rod.

Tethering by Aggregation and Growth, or the "T-BAG method," is a widely-employed application process in the field of surface chemistry, although it is prohibitively slow for anything but laboratory testing. To implement this procedure, one must first dissolve the chosen solute into an organic solvent with a relatively high vapor pressure, such as methanol, ethanol, toluene, acetone, or cyclo-hexane [6]. The surface to be coated is submerged in the solution and the volatile solvent evaporates away over the course of several days, allowing the solute to accumulate on the substrate. This procedure is highly reliable and requires little energy input. However, because the process takes several days, requires many liters of solution, and involves a precarious arrangement of upright slides, it is commercially impractical in its present form.

The Meyer Rod application technique is a simple, inexpensive, and efficient means of coating a substrate. First, the organic solution described in the previous paragraph must be sprayed upon the desired surface. Then the Meyer Rod - a long steel rod wrapped in a tight coil of thin wire mesh - must be rolled over the substrate, spreading the solution evenly over the glass and removing any excess liquid. This procedure, which requires less ODPa solution and time to implement than the T-BAG method, is much easier to replicate on an industrial scale.

Why Low- and Zero-Energy

Coating surfaces with phosphonic acid may be more time consuming than coating surfaces with Teflon, but it is also more environmentally sound. Teflon is a known carcinogen, and when sprayed onto tiles, glasses, or even cookware, it comes off over time [1]. Phosphonic acid, due to its similarity to common biological compounds, is harmless if consumed, and once it attaches to a surface, it is almost impossible to detach [3]. The laboratory method with the most success in attaching phosphonic acid to a surface is applying heat by placing the coated surface in an oven at 140° C for 36 hours [7]. Unfortunately, this process is not only time consuming but also expensive. We therefore decided to take a zero energy approach to attaching phosphonic acid. The cheapest available source of energy is natural sunlight, which is, of course, free. Buying land and building greenhouses are initial costs, after which the per-unit manufacturing process of coating surfaces with phosphonic acid is very cheap.

Another benefit of greenhouse heating is its carbon footprint of zero. A carbon footprint is the measure of how much greenhouse gas, usually measured in carbon dioxide, a process produces [8]. Since sunlight is simply radiation beaming down on Earth from the Sun, no gaseous byproducts are produced by harnessing this energy. Because waste gases from energy production, such as carbon dioxide, allow radiation from the sun to pass through them, but prevent reflected infrared radiation from escaping the earth's atmosphere, scientists believe this heat being trapped has led to an acceleration of the warming of our planet [9]. Ironically, the manufacturing process we propose is meant to use the original "greenhouse effect" without contributing to the global greenhouse effect. The success of Home Depot's new section of environmentally sound products and Whole Food's and Trader Joe's organic produces seems to prove that any disadvantages from a lengthy curing process could be offset through green marketing. Based on the green advertising potential and zero energy aspects, we decided to pursue this approach.

The Greenhouse

The sun emits visible, near infrared, ultraviolet, X-ray, gamma, microwave, radio, and longer wavelength thermal infrared radiation. Of these frequencies, only UV and lower reach Earth's surface. Efficient greenhouses are often constructed from materials with specific materials in order to maximize or minimize the absorption of certain radiation depending on what is being grown, produced or heated. While we were unable to determine what type of radiation would be ideal for the curing of phosphonic acid to a glass surface, we found research about the curing of other similar polymers that suggested UV absorbing, infrared reflecting surfaces would be ideal. Transparent materials that have these properties include pyrex, acrylic, polycarbonate, and other glasses with a lower iron oxide content. In addition, certain plastic glazes can be used in order to maximize these same effects. These include low density polyethylene and polyvinylchloride [10]. However, constructing our own greenhouse seemed out of the question. We did not think that purchasing these various types of glass or chemicals aimed at absorbing or reflecting certain types of radiation would be a productive use of time or funding. Rather, we decided to use the Hall of Sciences greenhouse at Drew University, which is constructed of ordinary window glass, in order to explore a variety of substrates that could be placed underneath the curing glass slides to maximize heat exposure and minimize time in an

ordinary glass greenhouse. Window glass transmits visible and high-frequency infrared light well, and blocks only UV frequencies above those our atmosphere absorbs.

In order to determine the best surfaces, we researched a variety of devices constructed to efficiently absorb solar radiation as well as the physics behind the transmission and reflection of light. For example, solar collectors absorb radiation onto a dark colored surface and heat water in copper or aluminum pipes in order to minimize temperature diminution. Further research suggested that dark surfaces are best as they concentrate heat and light by absorbing all frequencies of the visible spectrum. Often the best dark colored surfaces are dark insulated metals as they not only absorb all shades of the visible spectrum, but also reflect sunlight increasing exposure and heat permanence, while conducting heat [11]. While we hypothesized that dark metals would be the best surfaces, we also tested a variety of other surfaces based on reflectivity, heat conduction ability, color, three dimensional shape, and composition in order to determine which combination of attributes did indeed produce the best quality of slides in the shortest time.

Our Goal and Hypothesis

Since ODPa is a different sort of coating than Teflon, industry will require there to be a relatively cheap and efficient way to apply it to their products before it becomes common; current laboratory methods are not efficient. Our goal was to create this industry-friendly approach to ease the transition of ODPa into industrial use. The particular focus of our work was to find a low- or zero-energy approach to create the coating, to reduce costs to the manufacturer and hopefully the environment.

Our hypothesis is that the heat and light of the sun can be used to supply the energy for the dehydration reaction that bonds phosphonic acid to an oxide surface rapidly enough to be useful, and that the use of dark and/or metallic surfaces will improve the speed and quality of this curing. Furthermore, we also hypothesize that the Meyer Rod method of application will produce at least as effective a coating as the T-BAG method explored by previous groups.

PROCEDURE AND METHODS

Before we coated any slides, we cleaned the plain microscope slides in a hot water bath at 40°C and a hot ethanol bath at 30°C. We left the slides in the water for five minutes, then transferred them with cleaned forceps to the hot ethanol solution, where they stayed for two minutes. The slides were dried with paper towels, and allowed to air-dry before being coated.

Application

T-BAG: First, we prepared a mixture of ethanol and toluene in a 2:1 volumetric ratio, thus creating a solvent with both polar and nonpolar characteristics. We then deposited a scoopula-tip's worth of anhydrous octadecylphosphonic acid into one liter of the ethanol-toluene mixture to yield a 1.5 millimolar solution (assuming the volume of added ODPa to be negligible). Next, we poured the completed solution into a shallow dish and placed several clean glass slides "horizontally upright" in the vessel to maximize the surface area available for

deposition. After several days in the fume hood, the volatile ethanol and toluene solvent had evaporated away and a thick, consistent accretion of ODPA remained on every glass surface.

Meyer Rod: We first prepared the same ODPA solution that we used for the T-BAG method and sprayed it generously onto the glass slides, which were lying adjacent to one another on a flat plane. We then slowly rolled the Meyer Rod over the slides several times in opposite directions. The thickness of the coating applied was determined by the diameter of the thin wire; we selected a wire with a diameter of 03 mils (0.08 millimeters), which yielded a 0.27 mil (6.86 micron) solution layer [12]. Next, we allowed the substrate to dry in a fume hood for approximately five minutes (as compared to T-BAG's several day evaporation period). Finally, we marked the bottom left corner of each slide with a wax pencil to document the upward-facing surface.

Curing

We cured the slides under a number of conditions. Some, we cured in an oven at a range of temperatures, some we cured under UV light, some we kept at room temperature, and some we cured in the greenhouse at Drew University, which was the most complicated setup.

We set up a table inside the greenhouse containing 17 surfaces for the glass to cure on. The surfaces included a variety of plastics such as a black plastic serving tray, a blue plastic box, and a black foam bowl. We also used various paper products such as a black, waxed notebook cover and a sheet of notebook paper. Additionally, we tried glass and ceramics by covering slides with pyrex watchglasses and placing them on a ring stand base and on a steam evaporating pot. Our main surfaces, however, were metals. We used a piece of aluminum foil, a shoebox coated in aluminum foil, a metallic serving tray, a metallic bowl and a shoebox filled with small sheets of copper, galvanized steel, aluminum, titanium and titanium alloy. We tested this variety of surfaces in order to determine which underlayer produced the best quality of coating in the shortest time.

In order to accurately test the surfaces, we attempted to rule out variability of weather, temperature, and time duration. We did this by putting out Meyer rod and t-bag coated slides on the same day, on the same surfaces, and for the same amount of time. We also minimized the effect these variables had on our results by analyzing data using vector space modeling.

For each slide, we recorded the duration of time in the greenhouse, the average temperature in the greenhouse during that time, the ambient weather, the application process and the surface it was placed on. We kept the slides in labeled plastic cases in order to minimize possibility for loss, contamination, breakage, or mislabeling.

Cleaning Before Testing

Before we measured the slides, we cleaned them in a warm ethanol bath. We rubbed the slides between gloved fingers to remove dirt and residual ODPA. Using a pressurized air hose, we blew off most of the residual ethanol, and then baked the slides in a 130 degrees Celsius oven for five minutes to ensure that they were dry.

Testing the Coating – Contact Angle

We measured ODPAs attachment to the glass using a Ramé-Hart contact angle goniometer. An important characteristic shared by Teflon and the ODPAs replacement is hydrophobicity, or the ability to repel water [16]. The best way to test hydrophobicity is to measure the observed contact angle between the edges of a water droplet and the surface. For our purposes, a sufficiently hydrophobic piece of glass must have a contact angle of at least 85°. The goniometer uses a magnifying camera to view a single drop of water placed on a horizontal slide coated with the ODPAs (Figure 6) [16]. A computer program then calculates and records the contact angle of the water droplet.

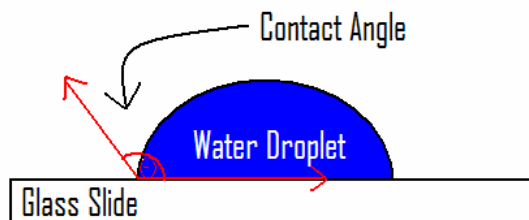


Figure 6. Goniometer view of a water droplet on a glass slide (contact angle in red)

We placed three 20 μ L drops onto each coated side of every slide, for three drops total on slides coated by a Meyer rod, and six total for T-BAG slides. Using the goniometer, we measured the contact angle on both sides of each drop, and used the average for each drop as a data point.

DATA ANALYSIS

We used an ANOVA test [13] to analyze our data, and determined that there was a statistically significant variation between samples ($P < .01$). All of the T-BAG samples except aluminum, galvanized steel, and titanium alloy had contact angles of less than seventy degrees, while the Meyer rod samples consistently had hydrophobicities greater than 70 degrees. Many of the Meyer rod samples had hydrophobicities greater than the oven-baked positive control. Among the Meyer rod samples, the aluminum foil box, ringstand, and metallic bowl had the greatest contact angles (Appendices C and D).

We then constructed a vector space model [14] using the dimensions of effectiveness, reliability, time, and energy efficiency and calculated “goodness” values (Appendix A). Using even dimension weighting factors, the aluminum foil box, the ring stand, and the metallic bowl had the greatest goodness vectors. They had larger magnitudes than the ironed samples, even though application via ironing took less time than the greenhouse application (Appendix E). When we changed the goodness formula to weight the variables more heavily, the aluminum foil box, the ring stand, and the silver bowl continued to have the greatest goodness values. However, when reliability was weighted more heavily, these three samples had the lowest goodness value, implying a steep trade-off between quality, time, energy and consistency (Appendices F, G, H, I).

Finally, we used Principle Component Analysis [15] through the statistical program Unscrambler to determine which variables most influenced our results (Appendix B). By analyzing the clusters of data points created by this method, we determined that the application methods and the heating methods contributed to the variation in goodness values (Appendix J). The ironed samples formed a separate cluster, while the T-BAG and Meyer rod samples formed a cluster each. A sub-cluster of the 72 hour exposure slides formed within the Meyer Rod cluster. Such sectioning behavior based on time indicates that exposure time was an important factor in determining goodness. Within the sub-cluster containing 72 hour exposure slides, clusters formed of slides on metal and slides in a shoebox. The short-term sector did not contain clear clustering among T-BAG, Meyer-rod, and iron-heated samples indicates that application technique corresponds with the goodness value. Clustering patterns also indicate that the greenhouse surface had a greater effect on the long-term samples than on the short term samples.

Additionally, we performed a few small-scale experiments to test one variable each. We placed slides at room temperature under UV lamps at several wavelengths, and found that they cured no better than controls left at room temperature, suggesting that UV light does little to cure ODPA.

CONCLUSIONS AND DISCUSSION

Sources of Error

As with any process, our method has several possible flaws. Contact angle analysis is very vulnerable to operator error, and our cleaning quality varied from slide to slide. Our coating procedures also varied over time: the solution for coating by T-BAG had a different concentration every time, and in the worst cases, the solution may have formed micelles.

The primary source of error in contact angle analysis is from smeared droplets. The droplet we lowered onto the glass was very small, only about two millimeters in diameter. This size made it difficult to carefully lower the droplet, as the operator's hand was liable to shake over a length much greater than the size of the droplet. If the droplet is lowered to the surface, and then the tip of the syringe is dragged sideways, rather than straight back up, the droplet often assumes an oblong shape, which results in an artificially low contact angle reading [16]. We hypothesize that this affected all the samples roughly evenly, and therefore the effect on our final conclusions is minimal.

An uneven coating on the slide surface, often resulting from T-BAG application, was also likely to create a false contact angle reading. If the droplet is lowered onto an area where one side is hydrophobic and one side is hydrophilic, then it tends to spread out over the hydrophilic section in a way that ignores the hydrophobicity of the other half. This may account for some of the T-BAG method's lower scores, but it also likely hid some of the unevenness of the T-BAG method, so it is still undesirable to use.

Past experimenters did not observe such poor results with the T-BAG method. For example, researchers using the same lab last year observed a "consistent contact angle of 95°," which is significantly higher than our findings for the same method [17]. We believe this

difference to be due to micelle formation in the solution used to coat the slides. All of our solutions are thousands of times that necessary to coat the surface, and, because small quantities of powder are difficult to handle, we put a comparatively large amount of ODPA into the solution. Since the molecule has a polar end and a non-polar end, we believe that the polar ends may have aggregated together, forming structures known as micelles.

Micelles are best known as formed by soaps in water, with the non-polar ends aggregating, but they can also form in oil, like our solution of ethanol and toluene [18]. Since the bonding ends of the molecule is the polar end, micelle formation would result in less bonding. Furthermore, micelles may have also simply stuck mechanically to the glass surface. When we cleaned the T-BAG slides, almost all of them had white deposits that were nearly impossible to remove. These deposits may have been formed by micelles. To make matters worse, as the solution evaporated, coating the slide, it became more concentrated, resulting in even worse micelle formation. The combination of these two effects almost certainly lowered the quality of the slides' coating.

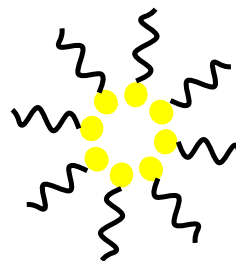


Figure 6: Micelle

Further room for error was in the cleaning of slides after curing. For accurate readings, these slides had to be thoroughly cleaned to ensure that their hydrophobicity resulted only from ODPA physically bonded to the glass, and not simply sitting on the glass. On more than one occasion, we sent a group of slides to be re-washed because their contact angles were unbelievably high. After washing a second time, the angles lowered to a value that, while still high, was believable. It is possible that other slides were similarly affected, but were not high enough to be selected for re-washing, artificially raising their quality. This effect should have affected slides at random, though, and should have little overall effect since we took many samples.

Though our methods had room for error, and the T-BAG results were almost certainly skewed, overall we believe our conclusions remain solid. From an applicability standpoint, the T-BAG method is inefficient, and, if other researchers' results can be used as a benchmark, our Meyer rod samples tended to score higher than the 95° found on T-BAG. Furthermore, most of the other errors affect random slides, leaving our conclusions about the practicality of curing outside of an oven relatively unharmed.

Areas for Further Research

While we were successful in many aspects, there is still a lot that needs to be done before the process would meet an industrial standard. The Meyer rod technique needs to be perfected in such a way that the coating is as evenly distributed as possible. The aluminum, ceramic ring stand, and metallic bowl surfaces seem to have the greatest potential for use if the industry is interested in maximizing effectiveness and energy efficiency and minimizing time used to produce ODPA surfaces.

Further research will need to be conducted to isolate the variables of each of these surfaces to determine which attributes are causing the differences in quality. The greenhouse

also poses issues on a larger scale as the strength of solar radiation varies throughout the year. The ideal setting for a factory of this sort would be near the equator in an area where daylight hours are maximum and cloudiness and rain are minimum. As this is obviously not always possible, perhaps a thermally engineered system for gathering and storing heat could be used to maintain a constant temperature in the greenhouse even when the weather is not ideal.

Additionally, when we placed the glass slides in the greenhouse directly on the surface, we did not consider the inefficiency of our surface use. In a large scale production, this process would require an extreme amount of area but little height (in order for all glass slides to be in the sun), thus requiring a vast space for curing. Further research should determine whether slides can be stacked or packed more tightly while maintaining the same standard of quality.

One final area of interest to the group is what exactly causes ODPa to cure. Though we believe we have ruled out UV light, our sample size was small, and our margin of error relatively large. Even if UV is not what cures it, another frequency of light could, or it could be heat. Determining exactly what factor causes curing will allow for much greater efficiency in research and in production.

Overall

We were able to find a low-energy application technique and zero-energy heating technique for applying ODPa. The Meyer rod application method was, overall, more effective than the T-bag application method due to the T-bag's uneven coating and low hydrophobicity, although flaws in the T-BAG application may have lowered the results. Meyer rod application, though, is still faster and more efficient, and can be applied in an industrial setting on large rollers. We also determined that the use of aluminum, ceramics and other metals as substrate surface materials enhanced the quality of the coating and minimized the time necessary to cure ODPa, according to our PCA analysis.

The prospects for ODPa in the future look bright. With only minimal future research it should be possible to find an energy, time and labor-efficient application process, allowing ODPa to replace PTFE in a wide variety of applications, and for ODPa to be used in other ways.

REFERENCES

- [1] Ross, Michael J., Ed. "Pristine Planet Newsletter." Pristine Planet. 10 May 2006. Pristine Planet. 10 Aug 2007 <<http://www.pristineplanet.com/newsletter/2006/05.asp>>.
- [2] Wingrave, James A. Oxide Surfaces (Surfactant Science). New York: Marcel Dekker Inc., 2001.
- [3] Nowack, Bernd. "Environmental Chemistry of Phosphonates." Institute of Terrestrial ecology 31 Jan 2003. 7 Aug 2007. <<http://72.14.205.104/search?q=cache:veNiDxPqIDcJ:www.ito.ethz.ch:16080/soilprot/staff/nowack/pdf/review%2520phosphonates.pdf+properties+of+phosphonates&hl=en&ct=clnk&cd=8&gl=us>>.
- [4] Gawalt, Ellen S. et al. "Self-Assembly and Bonding of Alkanephosphonic Acids on the

- Native Oxide Surface of Titanium ." Langmuir 17(2001): 5736-5738.
- [5] Biddle, Margaret M. "An Introduction to SAMs: Self-Assembled Monolayers in Organic Chemistry." The Organic Chemistry Division. 9 Oct 2001. Chemistry Department, University of Wisconsin-Madison. 3 Aug 2007. <<http://www.chem.wisc.edu/areas/organic/studsemin/biddle/biddle-abs.pdf>>
- [6] Kanta, A., R. Sedev, and J. Ralston. "The Formation and Stability of Self-Assembled Monolayers of Octadecylphosphonic Acid on Titania." Colloids and Surfaces A: Physicochemical and Engineering Aspects 291(2006): 51-58.
- [7] Gouzman, Irina et al. "Monolayer vs. Multilayer Self-Assembled Alkylphosphonate Films: X-ray Photoelectron Spectroscopy Studies." Applied Surface Science 600(2006): 773-781.
- [8] "What is a Carbon Footprint." Carbon Footprint. 19 July 2007. Carbon Footprint Ltd. 7 Aug 2007 <http://www.carbonfootprint.com/carbon_footprint.html>.
- [9] "The Greenhouse Effect." Liftoff to Space Exploration. 27 Mar 2002. NASA. 5 Aug 2007 <<http://liftoff.msfc.nasa.gov/academy/space/greenhouse.html>>.
- [10] Davis, Anthony, and David Sims. Weathering of Polymers. Essex, England: Elsevier Applied Science Publishers Ltd., 1986.
- [11] Pidwirny, Michael. "Solar Radiation." The Encyclopedia of Earth. 2006. 1 Aug 2007 <http://www.eoearth.org/article/Solar_radiation>.
- [12] Cohen, Dr. Edward D. "Meyer Rod Coater." Web Coating Blog. 27 July 2005. Association of Industrial Metallizers, Coaters, and Laminators. 8 Aug 2007 <http://www.webcoatingblog.com/blog/2005/07/Meyer_rod_coate.html>.
- [13] Kirkman, T. "ANOVA: ANalysis Of VAriance between Groups." Tools for Science. College of St. Benedicts. 2 Aug 2007. <<http://www.physics.csbsju.edu/stats/anova.html>>.
- [14] Bradshaw, Shannon. "Referencing Directed Indexing: Redeeming Relevance for Subject Search in Citation Indexes." 2003. Department of Management Sciences, the University of Iowa. <<http://www.springerlink.com/content/5hj073kcydn5901x/>>.
- [15] "Principal Component Analysis." CAMO Software AS. 2006. <<http://www.camo.com/rt/Resources/principal-component-analysis.html>>.
- [16] Li, W., and A. Amirfazli. "Design of Microtextured Superhydrophobic Surfaces: a Thermodynamic Analysis." Advances in Colloid and Interface Science 132(2007): 51-68.
- [17] Amrute, Sachin et al. "Can We Develop the New Teflon? Developing Coatings and Looking at Surface Molecular Dynamics." New Jersey Governor's School of the Sciences. 2006. New Jersey Governor's School of the Sciences. 9 Aug 2007. <<http://depts.drew.edu/govschl/NJGSS2006/Journal/TeamPages/Team2JournalPage.htm>>.
- [18] Moroi, Yoshikiyo. Micelles: Theoretical and Applied Analysis.

APPENDICES

Appendix A: Vector Space Modeling

The effectiveness of an application-heating technique is a function of four variables:

1. Hydrophobicity (180° - contact angle)- represented by H
2. Evenness of coating (standard deviation)- represented by E
3. Time of application (hours)- represented by T
4. Artificial energy input (Joules)- represented by J

A cumulative “Goodness” value was defined to provide a means for comparing the effectiveness of each application-heating technique across all four variables. Each application-heating technique was assigned a coordinate in four dimensional space (here the fourth dimension is not time, as in physical reality, but merely another variable direction to be taken). The “Goodness” value is defined as the inverse of the distance between the coordinate and the origin. The distance can be calculated using Pythagorean Theorem:

$$\text{Goodness} = 1/(\text{H}^2 + \text{E}^2 + \text{T}^2 + \text{J}^2)$$

However, this “Goodness” value would be biased because some variables have larger ranges than others. To reduce this bias, the measurements for each variable were set to a scale from 0 to 100, and the coordinates for each sample contained the scaled values [17].

Appendix B: PCA Analysis

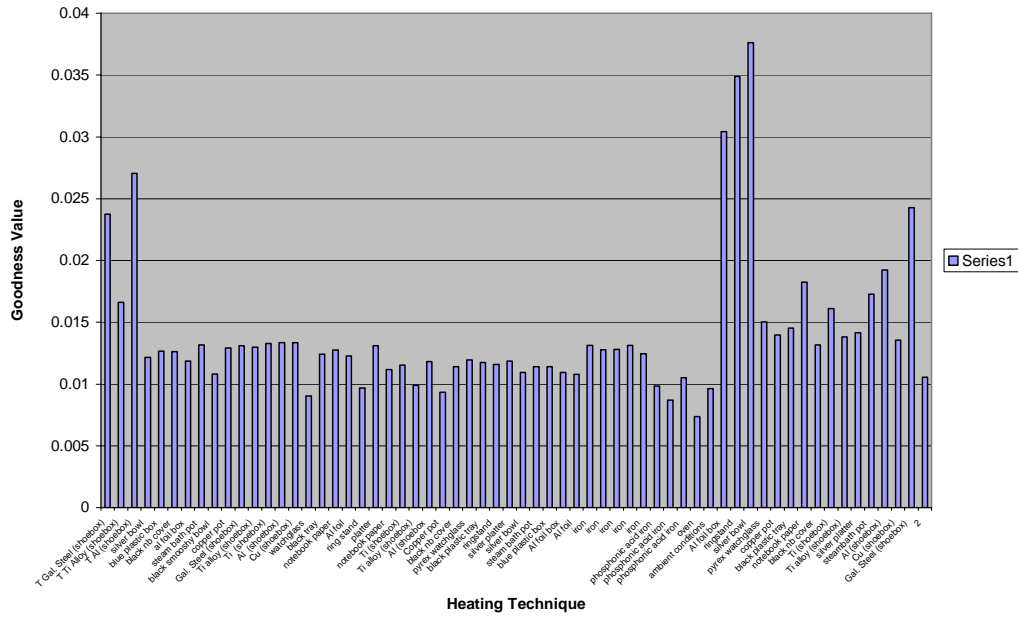
From the multi-dimensional vector-space, a matrix was created comparing the cosine between each pair of vectors. The cosine function provides a means of comparing the variation between any pair of sample-vectors. Cosine was calculated using the following function:

$$\text{Cos}(A, B) = \frac{\mathbf{A} \cdot \mathbf{B}}{\|\mathbf{A}\| \|\mathbf{B}\|}$$

The table was inputted into a Principle Component Analysis (PCA) program. PCA analysis condenses multidimensional data into a two-dimensional cluster diagram that can be used to evaluate the similarities and differences between sample sets. PCA essentially finds the 2-D slice within the multi-dimensional space that causes the points to be most spread out. Specifically, PCA maps the data in a multi-dimensional space based on the variance matrix. It then creates a number of perpendicular axes through the multi-dimensional space and condenses all of the points in the space to each line. The lines that contribute the most to the variation between points on the graph are considered the principle components. The two main principle components are used as the axes for the cluster diagram [14].

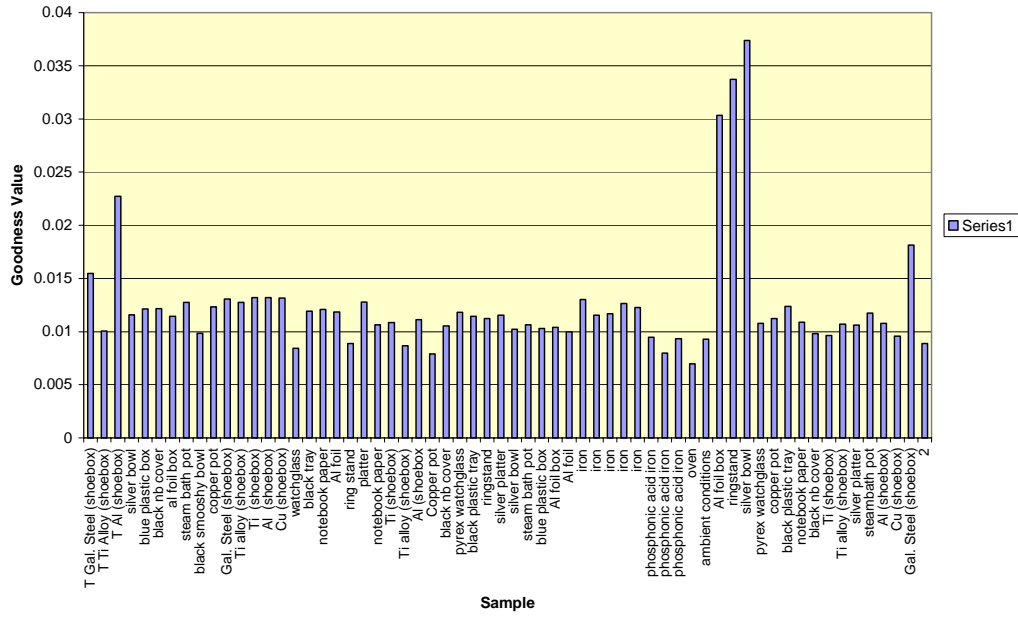
Appendix C

Industrial Effectiveness of Phosphonic Acid Bonding Techniques



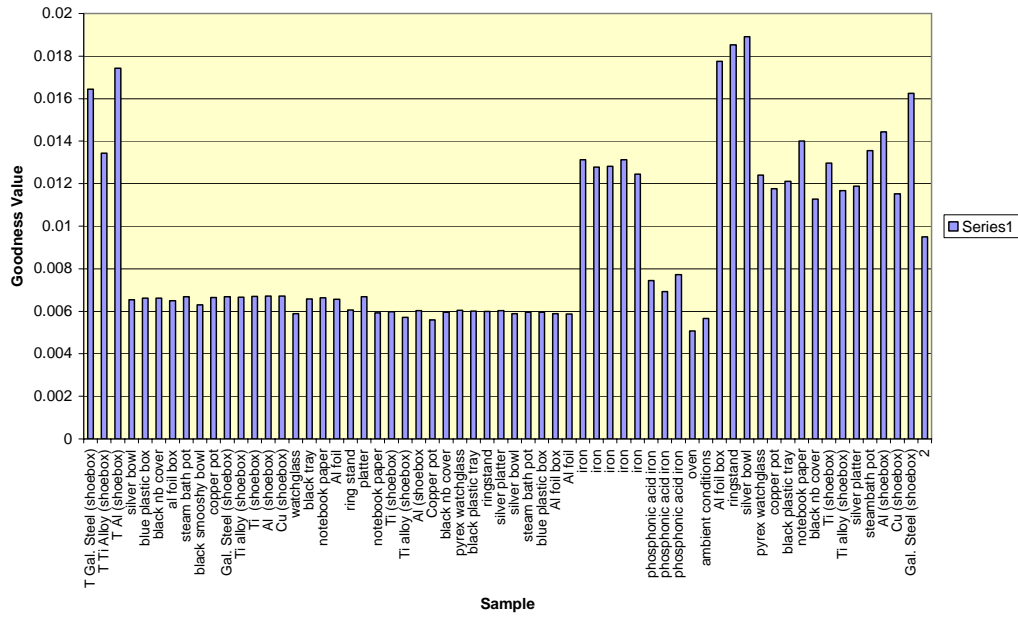
Appendix D:

Goodness Value: Emphasis on Effectivity of Coating



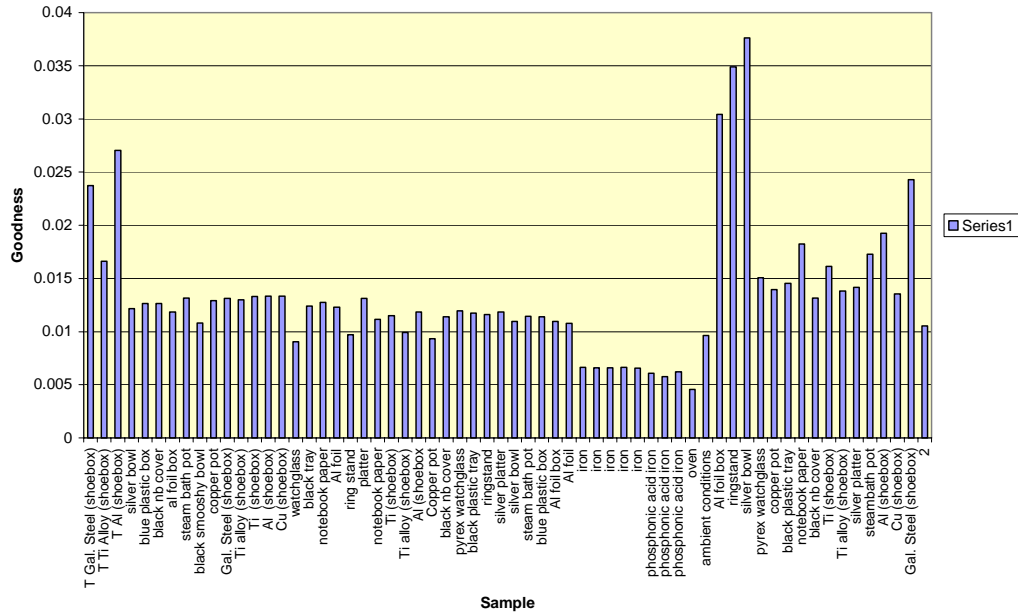
Appendix E:

Goodness Values with Emphasis on Time



Appendix F:

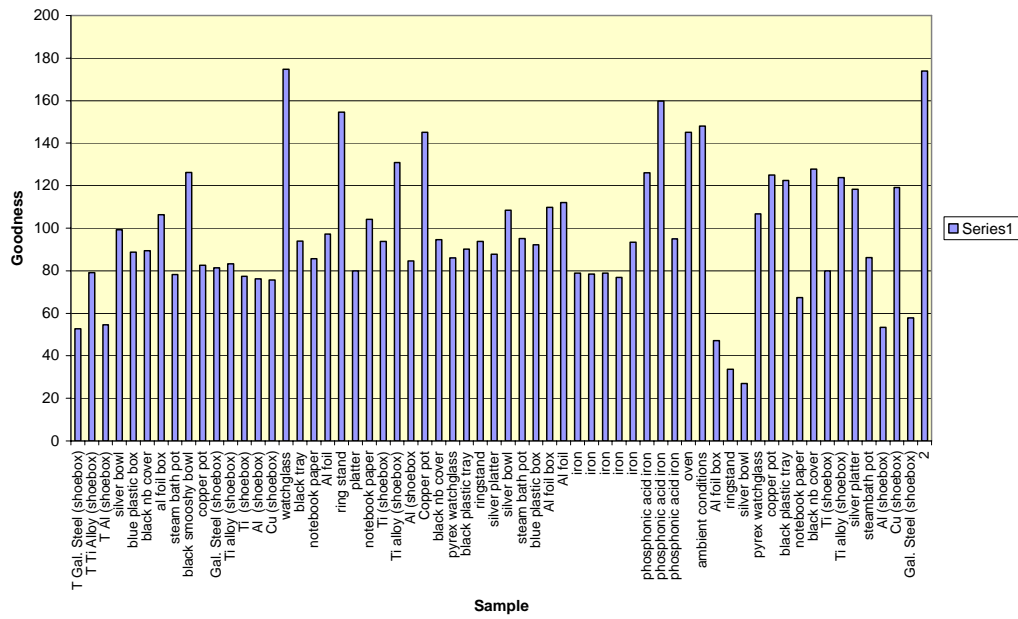
Goodness Value with Emphasis on Energy Efficiency



Appendix G:

Goodness Value with Emphasis on Reliability

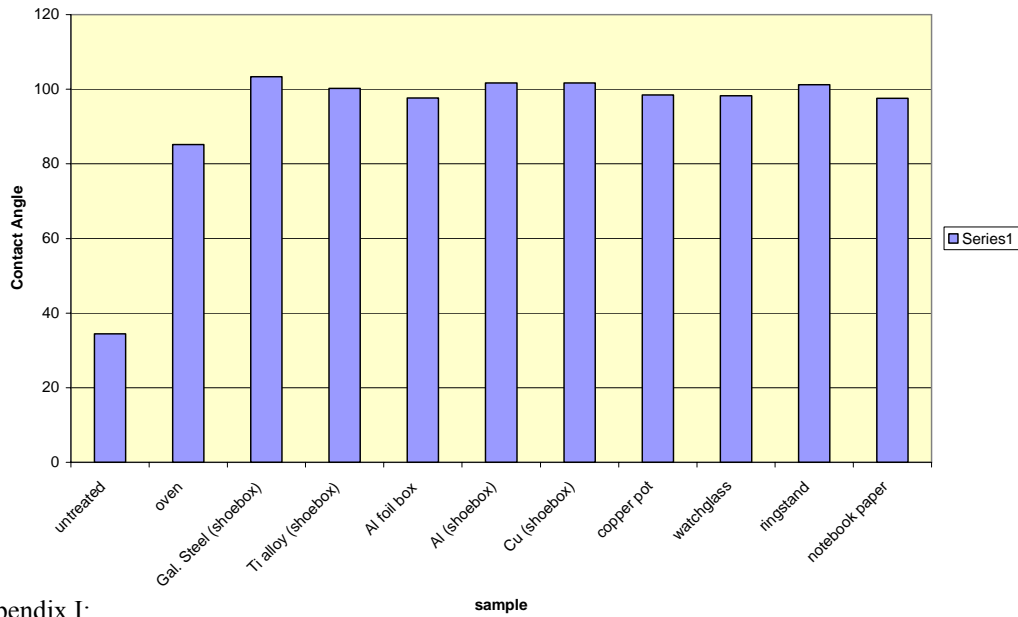
Formatted: Underline



Appendix H:

Formatted: Underline

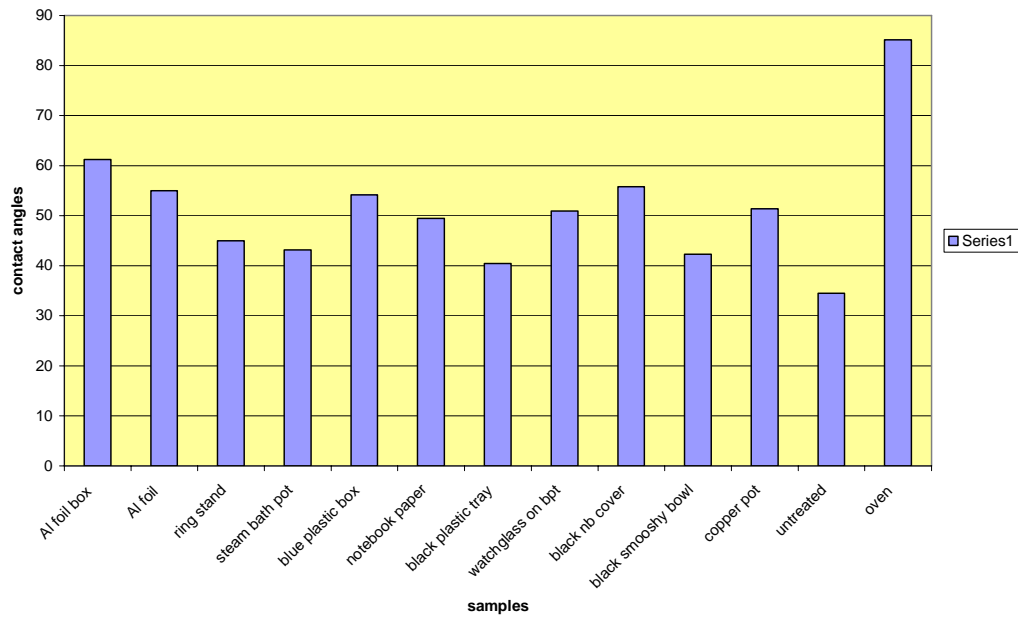
Hydrophobicity Using Meyer-Rod Application Technique



Appendix I:

Formatted: Underline

Hydrophobicity of T-BAG Samples After 71.25 Hours



Appendix J:

