

TRANSFORMING TEFLON®

A SYSTEMATIC INVESTIGATION OF HYDROPHOBIC MATERIAL COATINGS

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ABSTRACT

In this project, the hydrophobic and adhesive properties of two different phosphonic acids were investigated as potential replacements for Teflon®. Various application methods were tested in order to determine the most effective way of bonding these coatings to standard cookware surfaces. Additionally, primers were tested to better bond the phosphonic acid coatings to the surfaces tested in order to improve hydrophobicity and durability. Octadecylphosphonic acid (OPA) has been shown to have comparable hydrophobic properties to Teflon® and was tested alongside perfluorooctylphosphonic acid (P-FOPA), a coating that seemed promising due to its structural similarity to both Teflon® and OPA.

INTRODUCTION

Teflon®, also known as polytetrafluoroethylene (PTFE), has unique properties that give it the potential for many uses. It was first used in 1944 to coat the equipment needed to enrich the uranium used for the Manhattan Project because of its low coefficient of friction (between .05 and .20) and its resistance to most chemicals and compounds. PTFE is also a non-stick material, which is important in its role as a cooking surface. In addition, PTFE is both hydrophobic and oleophobic, meaning that it resists both water and oil. Another one of the properties that makes it desirable as cookware is its low heat dissipation factor. It can withstand temperatures up to 300°C for short amounts of time. PTFE can also resist damage from UV radiation and other normal weather conditions. Teflon® has played a role as insulation in the electrical industry, in the brake systems and oil filters of cars, and in countless other industries (1).

There are, however, some dangers associated with PTFE. In 2005 the EPA announced that perfluorooctanoic acid (PFOA), a common component of PTFE, was a possible carcinogen (2). The Environmental Working Group has also performed studies to back this claim by linking PFOA to multiple types of cancer (3).

Basics of Bonding Phosphonic Acids to Surfaces

One possible replacement for Teflon is octadecylphosphonic acid (OPA). Phosphonic acids such as OPA can bond to the surface of a metal by using the oxide surface as a bonding site. Metal surfaces oxidize forming attached μ -oxo groups and hydroxyl groups. However, since oxide surfaces are usually very inert, a strong source of heat is needed to catalyze the formation of covalent bonds between the phosphonic acid and the surface (3).

Some chemical coatings require a bifunctional linker to bond to particularly nonreactive surfaces (3). The structure of a bifunctional linker is shown in Figure 1.

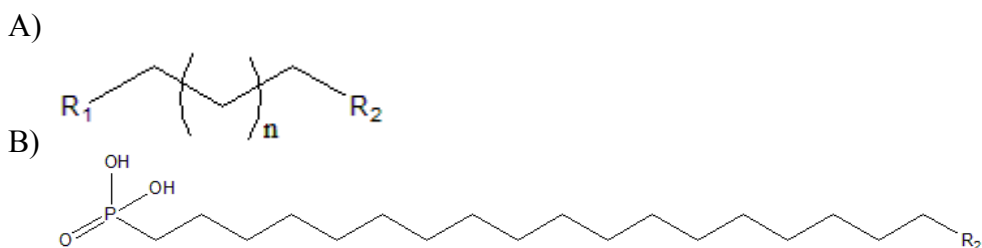


Figure 1 Figure 1A shows the phosphonate group in a typical bifunctional linker. Figure 1B represents the long hydrophobic chain that links both reactive groups together. In OPA, the R₁ group is a phosphonate group and the linker is 18 carbons long (3).

In bifunctional linkers, such as OPA, the phosphonate functional group at one end allows the linker to bind to the metal's oxide surface and the other functional group allows it to bind another molecule. This oxidation process is shown in Figure 2.

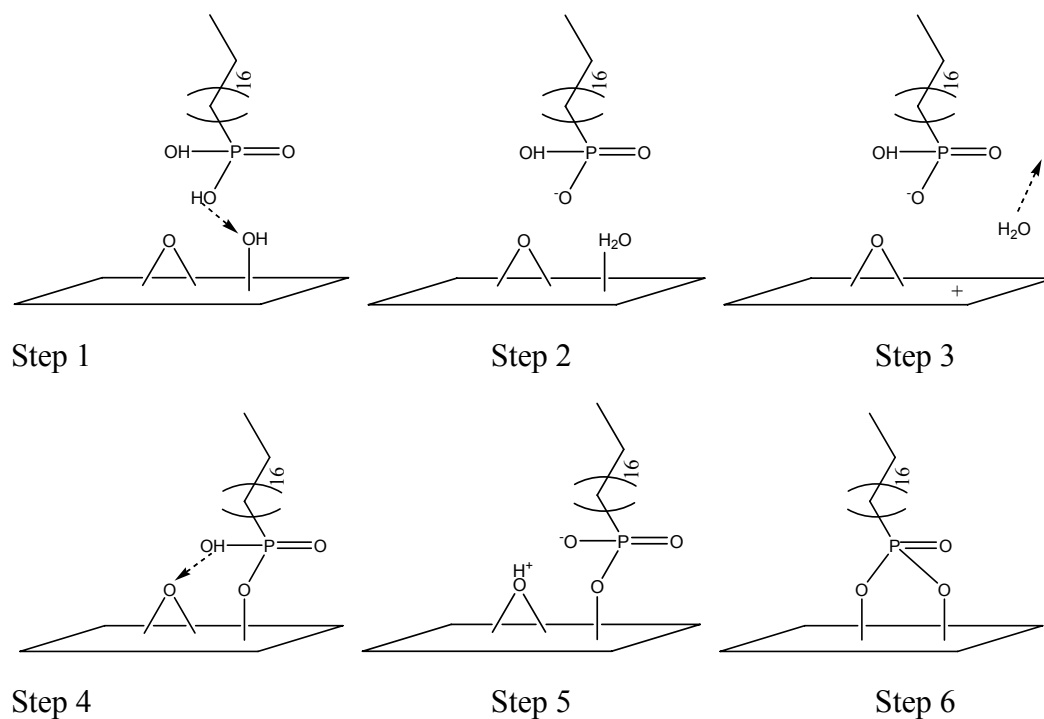


Figure 2 In Step 1, the hydrogen atom from the phosphonate functional group is attracted to the hydroxyl group on the surface, which it bonds to in Step 2 to form H₂O. In Step 3, the water molecule leaves the surface. In Step 4 the negative oxygen atom forms a bond with the positive surface. Another hydrogen atom from the phosphonate group bonds to the μ -oxo group in Step 5, and in Step 6 the negative oxygen atom from the phosphonate group forms a bond with the hydroxyl group, forming two bonds between the phosphonic acid and the surface (4).

Since phosphonic acids are diprotic, they can form strong bonds with oxide surfaces that monoprotic acids cannot (4).

Problems with OPA

One problem with OPA is that the oxidation process is particularly inefficient. The rate determining step for OPA is the dehydration of water, which requires constant heating for 18 hours at 120°C (4). Another issue with OPA is that with present methods of application it is not significantly more durable nor is it more marketable than Teflon.

Purpose

The purpose of this project was to explore possible chemically bonded replacements for PTFE that are just as durable while also being safer.

Apart from testing compounds to create safer cookware, another purpose of this project was to test alternative ways of improving phosphonic acid coatings that can be used in medicine. In orthopedics, titanium is used in bone and joint implants. However, the surface of titanium does not facilitate bone growth, which can create a gap between the implant and the surrounding tissue that is vulnerable to deadly infections such as MRSA. The solution to this problem is to integrate the bone and implant. This integration requires a surface coating that is conducive to bone growth, however, these coatings cannot be directly bonded to the titanium surface (3). Therefore, a linker is needed to create a compatible surface. Using a phosphonic acid as a primary coating, another linker can then be bonded to the phosphonic acid, and that linker can bond to certain coatings that facilitate bone integration.

Project

Several experiments were conducted in this project. The first of these experiments examined fluorinated phosphonic acid (P-FOPA) as a possible replacement for PTFE by applying it to various surfaces and testing its durability. These results were compared with the results of durability of a comparable and previously established compound, OPA. Both of these phosphonic acids have the ability to chemically bond to the surface of the materials and should not flake off with repeated use. The second experiment examined the use of primers in between the phosphonic acid and the metal to investigate an alteration of the oxide surface to change the packing and efficiency of the coating. The first primer, dimethyl phthalate, is a common insect repellent that features two ester groups that may interact with the hydroxyl or μ -oxo groups [4]. Next, tantalum-2-ethylhexoxide was used, which may pose a safety concern with the use of tantalum [5]. Tantalum ethoxide is considered a metal salt of ethanol, and is known in the production of oxide films of metals [6]. Tantalum (V) chloride is another tantalum based primer that hydrolyzes readily and releases HCl upon such a reaction. Its strong electrophilic properties may prove useful as an oxide coater [7]. Another primer, hydroxyl terminated polydimethylsiloxane, may increase the effectiveness of a phosphonic acid coating because its hydroxyl groups will create more bonding points for the phosphonic acid [8]. Similarly, polydimethylsiloxane-*co*-dimer acid, bis(perfluorododecyl) terminated is another primer that utilizes the polydimethylsiloxane, PDMS, polymer to coat oxide surfaces [9].

PROCEDURE

Differing methods of applying phosphonic acids and their effect on durability

Preparation of Samples

Sanded aluminum sheets and stainless steel 316L alloy cylindrical chips as well as pyrex slides were washed in a hot ethanol bath (70° C) for seven minutes. The slides were then transferred to a hot water bath for two minutes. OPA was dissolved in ethanol to produce a 1 millimolar solution. The P-FOPA was dissolved in 50% ethanol 50% chloroform solution to make a 1 millimolar solution.

Application of Coatings

The OPA and the P-FOPA solutions were sprayed and dropped respectively on each set of samples. A 3 micron Meyer rod was dragged repeatedly across each surface. The samples were dried at room temperature. Constant heat was applied for one minute using a household iron in order to promote covalent bonding. The OPA and P-FOPA coatings were reapplied and ironed on to double-coat the surface. Contact angles were measured using a Rame-hart Instrument Co. goniometer and DROPimage CA software (see Appendix A for method). A second set of samples was baked at 130 °C for over 24 hours. A third set of samples was coated, half of these with OPA and half with P-FOPA, and placed under an infrared lamp for 90 minutes. Aluminum foil was placed under the samples to ensure even heating. A fourth set of samples was coated and subjected to a heat gun at 316 °C for one minute. This batch was cooled in circulating air for 30 seconds. Contact angles were measured for each set to determine the most effective method of application.

Durability Testing

OPA and P-FOPA coated samples were scrubbed with steel wool for 10 seconds to test their degree of covalent bonding. A third set of samples was placed in an oven at 250 °C for one hour to measure the effect of heat. The samples were washed in an ethanol bath for 5 minutes. A fourth set of samples was washed with a sponge and handsoap for a standard time. Contact angles were measured after each test in order to determine which coating proved more durable.

Applying and testing the durability of primers

Preparation and Application of Primers

A few micrograms of each of the six primers were added to six separate 20 mL test tubes of ethanol. Each primer was then sprayed onto three pieces of sanded down aluminum that had been washed in ethanol. A 10 micron Meyer Rod was rolled over the sprayed aluminum pieces. The Meyer Rod was washed in the ethanol solvent before each application. The ethanol from the ethanol and primer mixture was allowed to evaporate (approximately 30 seconds). One batch of aluminum pieces was placed in an oven at 120 °C and left to bake for 30 minutes. The metal was allowed to cool to room temperature and then sprayed with OPA. The aluminum was again dragged with a Meyer Rod. These were placed in the oven and allowed to bake for 48 hours. A second batch of aluminum was prepared except the OPA was ironed on for two minutes. A third batch of aluminum was prepared as well but the primer was ironed on for two minutes and then the OPA was ironed on for an additional two minutes. The purpose of the three different

methods of application is to determine which method produced the best hydrophobic quality for the primer. Contact angles were measured for each batch, as explained in Appendix A.

Durability Testing

Each of the three previous batches of aluminum was washed in ethanol. Contact angles were measured again. The batch of aluminum in which the primers had been baked on and OPA ironed on was washed using a generic soap cleaner and warm tap water. The aluminum was allowed to dry and contact angles were measured.

Scanning Electron Microscope (SEM)

Aluminum and stainless steel samples coated with OPA and P-FOPA were observed using a Topcon ABT-32 scanning electron microscope. Control samples of aluminum and stainless steel with no coating were also tested. Each sample was observed at 800x magnification using 15 kV and a working distance of 10 cm.

RESULTS AND DISCUSSION

Experiment 1

Contact angles indicate the degree of hydrophobicity of the surface being tested. A surface that produces an angle above 90° can be classified as hydrophobic. Initial contact angles were obtained from untreated glass, aluminum, and stainless steel as well as from single layer coatings with OPA, P-FOPA, and PEBP on all the materials tested. The contact angles on the raw untreated surfaces were relatively low because these sanded surfaces were hydrophilic. The PEBP coating did cause an increase in contact angles compared to the bare surfaces, but they were far below the levels of PTFE (contact angle 110°) (10) and OPA, previously established as a viable replacement for PTFE (11). Consequently, PEBP was no longer tested for durability, as it proved an ineffective replacement for PTFE. OPA and P-FOPA yielded similar results to each other on both glass and aluminum, but P-FOPA proved to be a significantly better coating on stainless steel.

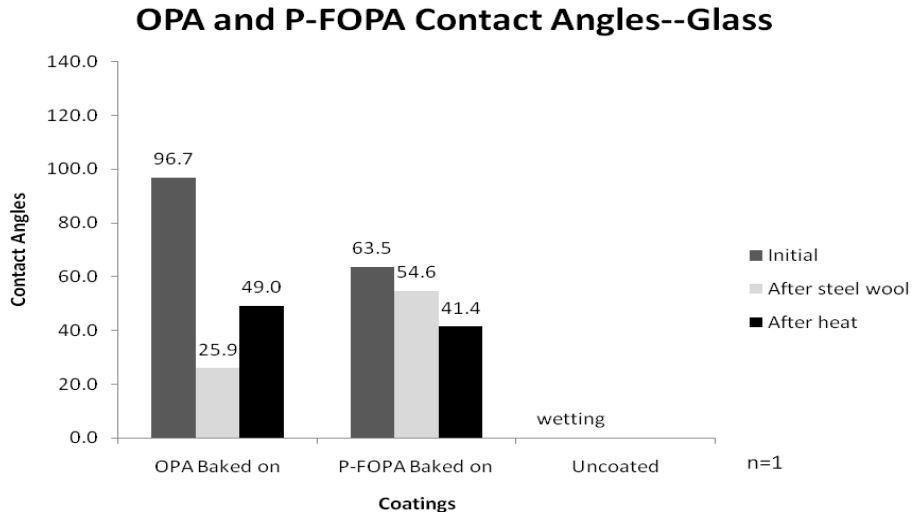


Figure 3 This graph compares both the hydrophobicity and the durability of glass coated with OPA and P-FOPA.

Figure 3 shows the contact angles obtained from glass coated with baked-on OPA and P-FOPA before and after the heat and steel wool durability tests. The contact angle for OPA was 29.5° higher than that of P-FOPA before the steel wool test; however, the P-FOPA withstood this test better than the OPA. They both performed equally on the heat test. Also, it can be seen that the OPA showed more consistent results than the P-FOPA.

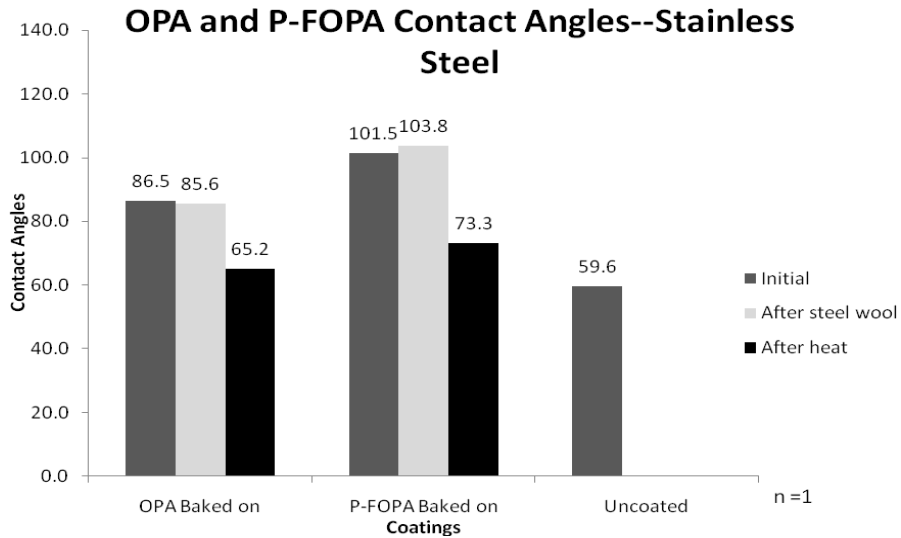


Figure 4 This graph compares both the hydrophobicity and the durability of stainless steel coated with OPA and P-FOPA.

Figure 4 shows that stainless steel yielded extremely high contact angles when coated with baked-on OPA and P-FOPA before and after the heat and steel wool durability tests. The OPA showed better initial results before the steel wool test, but neither coating endured the test well. This may have been due to the strength of the steel wool in that it was removing the actual

surface of the metals rather than just the coatings. The P-FOPA showed better initial results before the heat test, but did not withstand the test as well as the OPA did. Again, the OPA treatment showed more consistent results.

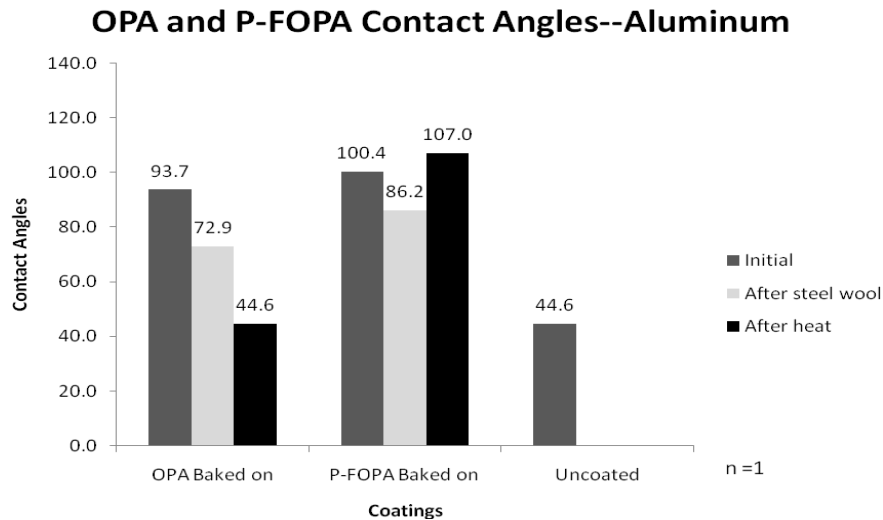


Figure 5 This graph compares both the hydrophobicity and the durability of aluminum coated with OPA and P-FOPA.

Figure 5 shows that the P-FOPA treatment had significantly better contact angles overall when compared to the OPA treatment on aluminum. The aluminum coated with P-FOPA had better initial contact angles, but the OPA better withstood the steel wool test, while the P-FOPA better withstood the heat test. In all cases the P-FOPA angles were higher than those of OPA. These results may be due to the fact that P-FOPA is fluorinated whereas OPA is not.

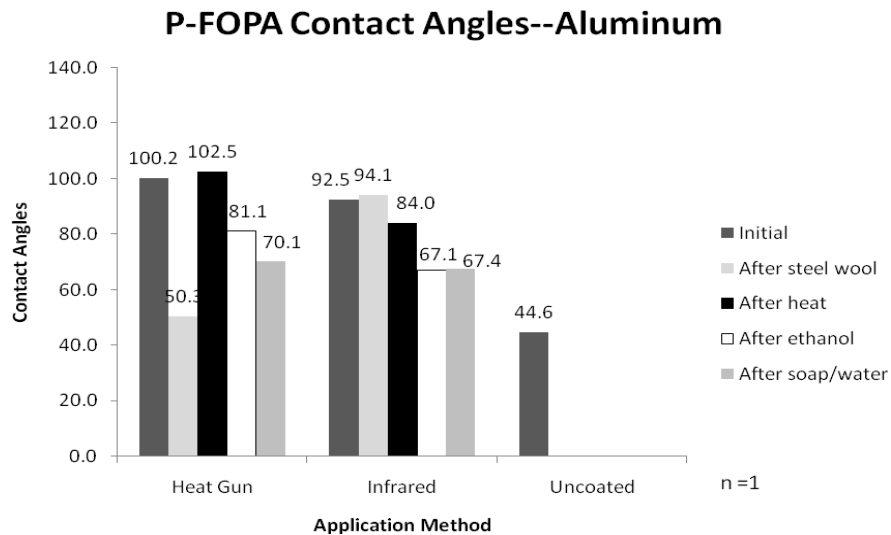


Figure 6 This graph compares the durability and hydrophobicity of P-FOPA applied with either a heat gun or an infrared lamp on aluminum.

The different application methods and heating processes did affect durability to some extent. Figure 6 shows the durability of P-FOPA on aluminum when a coating was applied using the heat gun or infrared. In general, both the heat gun and infrared methods caused the contact angles of the aluminum to decrease. With the steel wool test, the heat gun application performed very poorly, but overall the contact angles decreased the same amount. The glass samples had similar results in that both the heat gun and infrared lamp applications showed slight decreases in contact angles. However, the heat gun method created much higher initial contact angles on glass than did IR. Overall the data showed that the application method did not really affect durability as generally these methods performed similarly in each durability test.

Experiment 2

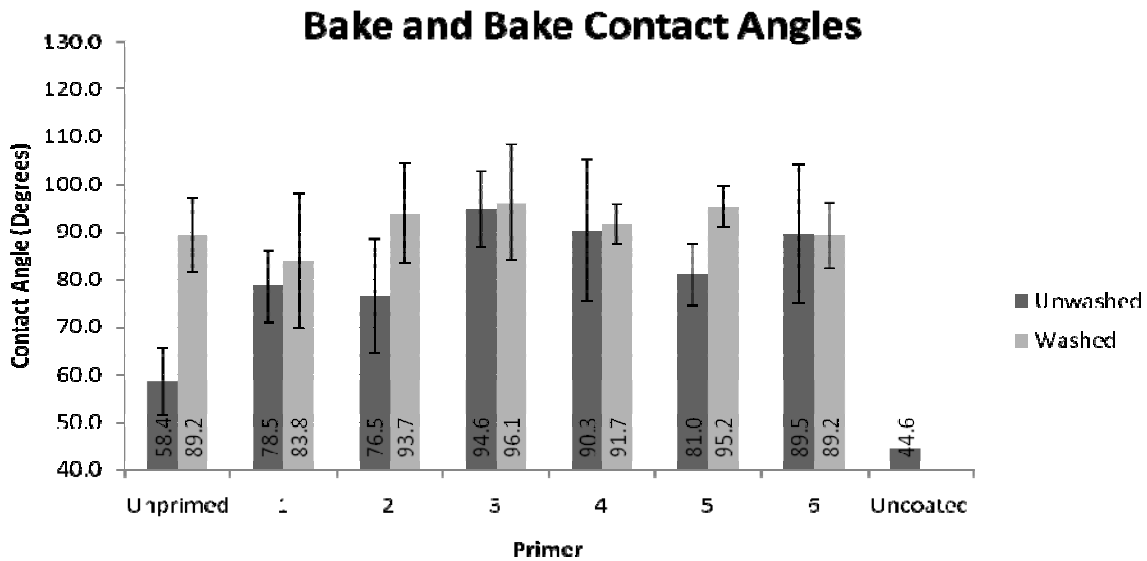


Figure 7 This application method entailed baking on the various primers and OPA. This graph also includes uncoated aluminum and aluminum coated OPA. The graph compares samples unwashed, and washed with ethanol. (mean, n=3) 1=Diethyl Phthalate, 2=Tantalum(V) 2-Ethylhexoxide, 3=PDMS-PFDD (Polydimethylsiloxane-co-dimer acid, bis(perfluorododecyl) terminated), 4= PDMS-OH (Polydimethylsiloxane hydroxyl terminated), 5=Tantalum (V) Ethoxide, 6=Tantalum (V) Chloride.

While both unprimed and primed coatings produced contact angles greater than uncoated aluminum, the bake and bake application method did not yield the best results when compared to bake and iron, and the iron and iron methods. This can be seen in figures eight and nine. Additionally, the baking of OPA onto the oxide surface did not seem like an effective bonding method because it yielded extremely variable contact angles. It is also important to note that technical error and lack of repetition in testing could contribute to the variability in the contact angles. Nevertheless, this application method demonstrates that the use of primers increases the mean contact angles of the oxide surface. The polydimethylsiloxane-co-dimer acid, bis(perfluorododecyl) terminated primer features the greatest mean contact angles. Interestingly, contact angles increased after the ethanol wash. This means that multi-layers of OPA were formed from extended time in the oven. Multi-layers consist of multiple levels of OPA

molecules that aren't bonded very well. These formations of OPA aren't very well packed, and aren't as hydrophobic as a mono-layer. When the multi-layers were washed off, a better ordered mono-layer was left.

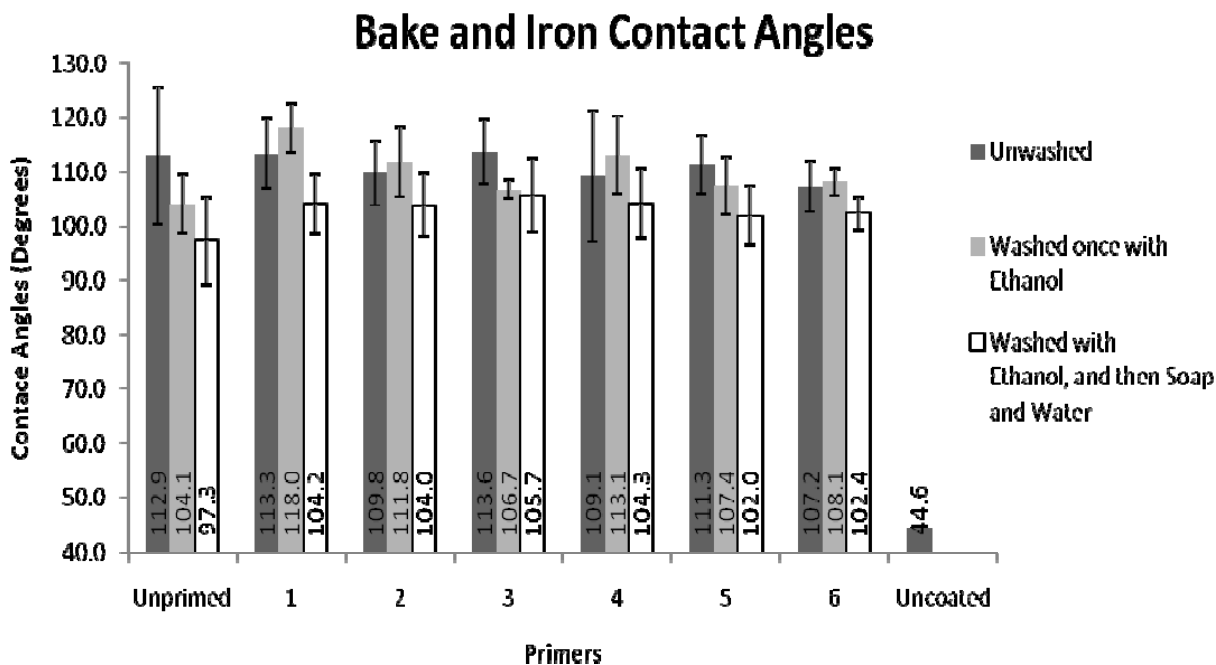


Figure 8 These samples had baked on primers and ironed on OPA. The graph contains contact angles of samples when unwashed, after an ethanol wash, and after a soap and water wash. (mean, n=3) 1=Diethyl Phthalate, 2=Tantalum(V) 2-Ethylhexoxide, 3=PDMS-PFDD (Polydimethylsiloxane-co-dimer acid, bis(perfluorododecyl) terminated), 4= PDMS-OH (Polydimethylsiloxane hydroxyl terminated), 5=Tantalum (V) Ethoxide, 6=Tantalum (V) Chloride.

Figure 8 shows that OPA increases the hydrophobicity of the surface, and although the use of primer does not seem beneficial before washing, it clearly produces higher contact angles after washing. The retention of these high contact angles on primed phosphonic acid surfaces over unprimed surfaces indicates that the use of primer encourages more thorough chemical bonding of the coating. After the second wash, the polydimethylsiloxane-co-dimer acid, bis(perfluorododecyl) terminated primer demonstrates the greatest mean contact angle and features a comparatively low standard deviation. This indicates great consistency in the performance of this primer.

Iron and Iron Contact Angles

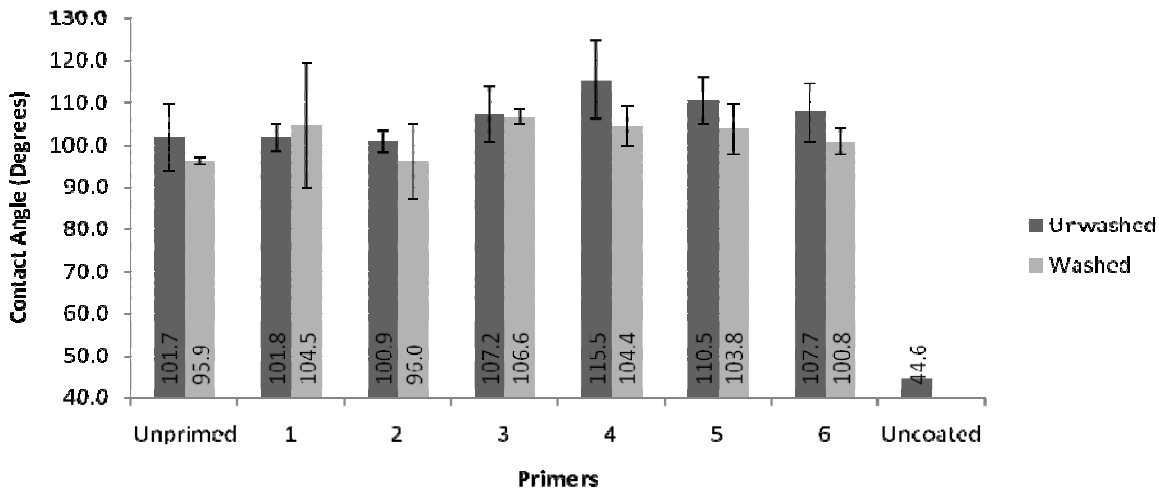


Figure 9 This application method involves ironing on ironing on both the primer and the coating. (mean, n=3) 1=Diethyl Phthalate, 2=Tantalum(V) 2-Ethylhexoxide, 3=PDMS-PFDD (Polydimethylsiloxane-co-dimer acid, bis(perfluorododecyl) terminated), 4= PDMS-OH (Polydimethylsiloxane hydroxyl terminated), 5=Tantalum (V) Ethoxide, 6=Tantalum (V) Chloride.

Both the unwashed and washed contact angle results displayed means significantly lower than the previous two application methods. Even though the contact angles still remained higher than uncoated aluminum, their lower means indicate that the OPA may not have fully bonded to the oxide surface. Therefore, this application method seems least optimal in both medical and industrial conditions.

It seems as though the most promising application method is the bake and iron method. It yielded high contact angles, and was very fast. The bake and bake method is also effective after washing, however the time necessary to follow the method makes it inefficient for industrial use. The bake and bake method showed the greatest durability, which makes it appropriate for medical implants. The iron and iron method showed the least durability, meaning that the OPA isn't bonded very well, making this method a poor choice for coating surfaces.

The data from the three application methods suggests that the primer polydimethylsiloxane-co-dimer acid, bis(perfluorododecyl) terminated, features the most consistent results. It produced OPA coatings with some of the highest contact angles. Diethyl Phthalate is viable for industrial applications because of its evident hydrophobicity, even after multiple washings. Its ease of solubility makes it more useful for large scale production. On the other hand, tantalum (V) ethoxide seems most appropriate for medical use. The expense of tantalum deems it rather inefficient for large scale production, but it bonds effectively to both oxide surfaces and OPA.

Experimentation focused on using primers to increase the speed of coating application and the durability of the coating. Both durability and hydrophobicity need to be improved upon

in order to create a coating that meets industrial standards of production. An effective primer should bond to the metal's oxide surface easily and quickly, and also bond with phosphonic acid better than the metal would. Tantalum ethoxide stood out as an effective primer due to its high and consistent results, and also due to its effective bonding mechanism. Ethyl phthalate stood out as a viable industrial option due to its positive results. It is already used in industry in plastics manufacturing and is fairly cheap. Finally, PMS-PDF displayed the most consistent results out of all the primers, and was therefore selected as a viable option for any application.

SEM Microscopy

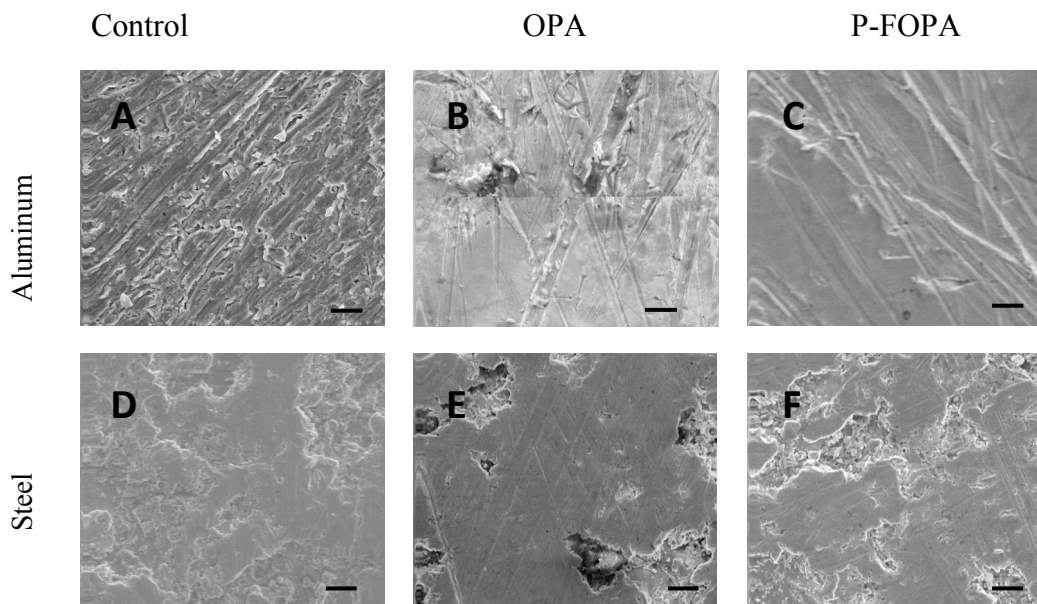


Figure 10 All samples were observed at 800x magnification. A: uncoated aluminum. B: aluminum coated by OPA. C: aluminum coated by P-FOPA. D: uncoated 316L stainless steel. E: 316L stainless steel coated by OPA. F: 316L stainless steel coated by P-FOPA. Scale 10 μm .

While contact angles played a significant role in the results of the experiment, images from a scanning electron microscope helped to verify the existence of molecular coatings on the material surfaces. The images in Figure 10 show the surfaces of stainless steel and aluminum samples before and after coating with OPA or P-FOPA. In addition to providing a contrast between uncoated and coated metals, the images reveal differences in the molecular appearances of the surfaces of the metals – aluminum and stainless steel – and differences between the coatings, OPA and P-FOPA. Uncoated stainless steel appeared to have a rough surface, which means that it had more surface area for the primers and coatings used in this experiment to bond to. Coatings of OPA and P-FOPA showed up in SEM imaging, making the surface of the aluminum appear more smooth. P-FOPA appears to have created an even smoother surface on aluminum, which could be either because of the molecular nature of the coating or because of error and variability in coating technique. Uncoated stainless steel appeared less rough and striated than uncoated aluminum. Though the surface of the coated steel did not necessarily

appear more smooth, the existence of the coating bonded to the surface is apparent from the pictures.

CONCLUSION

When the best coating (P-FOPA) was combined with each of the best primers (diethyl phthalate and tantalum ethoxide), the results were unexpected. Contrary to expectations, the use of primers prior to coating did not universally improve the hydrophobicity of the samples. The only samples for which the primers improved the hydrophobicity were the 316L stainless steel discs. The hydrophobicity of the glass and the aluminum decreased substantially when primers were used. A possible explanation is that the combination of primers and coatings reacts better with alloys than with samples consisting of only one metal. In the future, we would like to investigate the reasons why the coatings interacted so poorly with the primers when they were applied to the aluminum and the glass.

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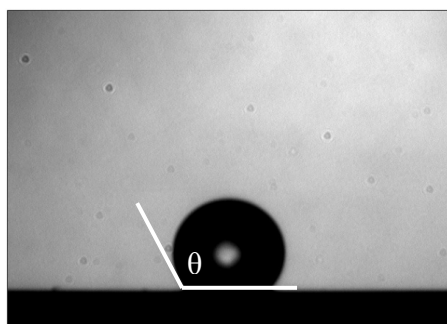
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APPENDIX A

Testing for Hydrophobicity (Contact Angles)

To test how well the samples repelled water, a Ramé-hart Instrument Co. goniometer and the DROPimage CA program were used to determine the contact angles for each sample. The contact angle is the angle formed by the tangent to the bead of water at its intersection with the surface (11). To perform the contact angle tests, a Hamilton Co. Inc. Microliter #705 syringe was used to place 5 μL droplets on each sample. The DROPimage CA program was then used to take pictures of each sample and to record the contact angle for each sample.

The picture below demonstrates how the contact angle is measured on a water droplet:



316L stainless steel coated with P-FOPA applied using heat gun. Prior to durability tests.