

Articles

Unusable Pretreatment of Steel and Zinc Surfaces Based on Phytic Acid

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The formation of a conversion layer for corrosion protection based on phytic acid (PA) solutions is described several times in the literature. The promising results induced us to verify the performance of PA based conversion layers as pre-treatment for organic coatings. The spectroscopic and optical analysis with infrared spectroscopy, atomic force microscopy, and scanning electron microscopy of the generated layer strengthened the hypothesis of a corrosion protective layer. Furthermore, the electrochemical analysis with cyclic voltammetry supported it but the results of the electrochemical impedance spectroscopy provided a first hint of an instable layer. Unfortunately, all kinds of tested conversion layers based on PA with and without a combination with molybdate increased the delamination of an applied coating and accelerated the corrosion process in the salt spray test. Therefore, all investigated PA based conversion layers are not suitable as pre-treatments for organic coatings.

1 Introduction

Corrosion is one of the greatest concerns for modern economies. The annual damage by corrosion causes a loss of 3–4 % of the U.S. GDP.^[1] To prevent corrosion, there are several methods on the market. In particular, conversion coatings are used with high success ever since the introduction of phosphate coatings.^[2] Besides their good corrosion protection, many established conversion coatings are harmful to humans and environment.^[3] Due to this fact there is a high need for ecological and sustainable alternatives. Phytic acid (PA) is a “green” option for future conversion coatings and has been proposed as a raw material for conversion layers in several papers in the last decade.^[4–7]

Phytic acid and its salts are used in many of our daily life products, e.g. cosmetics and water treatment.^[8] Naturally occurring PA is contained in beans, brown rice, corn, sesame seeds, and wheat bran.^[9] In the last years, novel production methods have been developed so that today PA can be easily extracted from rap filter cake.^[10] Phytic acid consists of an inositol ring structure which is esterified with phosphoric acid. Up to twelve hydrogen atoms can be removed. Metals can build strong chelate complexes with the active acid groups (Figure 1).

To verify the performance of conversion layers based on PA,

two strategies have been pursued:

1. Optimization of a conversion layer based only on PA and testing of the corrosion protective properties with an organic coating (clear coat) in a salt spray test.
2. Optimization of a conversion layer based on PA and molybdate^[7]/tungstate and testing the corrosion protective properties with an organic coating (epoxy based coating) in a salt spray test.

The structure and the corrosion resistance of PA conversion coatings on mild steel were observed at different pH values. The conversion coating was optimized with a leveling agent and molybdate as corrosion inhibitor. Reflection-absorption infrared spectroscopy (RAIRS), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) were used for characterization and verification. The film thickness was estimated twice via a gravimetric method and based on the interference color of the conversion layer. For the evaluation of the corrosion resistance, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and the salt spray test (SST) were used.

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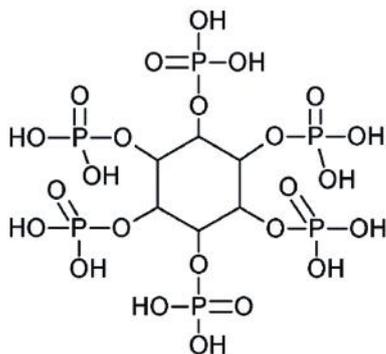


Figure 1: Chemical structure of PA, C₆H₁₈O₂₄P₆.

2 Experimental

2.1 Materials

The steel used in this study was mild steel with the classification DC04 (EN 10130) and the following chemical composition (wt%): C, 0.08 %; P, 0.03 %; S, 0.03 %; Mn 0.4 % (Krüppel, Germany). PA was used with a concentration of 50 wt% in water. Analytical purity grades of sodium hydroxide, potassium nitrate, ammonium heptamolybdate, and sodium tungstate were used for solution preparation. All chemicals were purchased from Sigma-Aldrich. Sokalan 64P as a leveling agent was purchased from BASF SE. All solutions were prepared with deionized water. For comparison, phosphate steel sheets (Chemetall) were used. Mild steel was cut into 110 x 65 x 2 mm samples. For the second series, steel, zinc coated steel and phosphate steel sheets used in the size 100 x 200 mm. Before the metal sheets were immersed into the PA solution, they were cleaned as followed:

The samples were wiped with ethanol and then ultrasonically washed for three minutes in deionized water at room

temperature. At the end they were wiped again with isopropanol.

2.2 PA Conversion Coatings

PA Layer

The PA solution (50 wt%) was diluted with deionized water to a 5 wt% solution. In the experiments, the different pH values (2, 4, and 6) were adjusted with sodium hydroxide. Potassium nitrate was added as a promoting agent (2 g/L). For the modification trials, Sokalan VA 64P was incorporated as a leveling agent (L) (1500 ppm). To achieve better corrosion properties, the inhibitor ammonium heptamolybdate (Mo) was used (1 wt% based on PA content). The test pieces were immersed for 30 minutes in the PA solutions (Table 1). The temperature of the solution was set to 35 °C.

Table 1: Experimental Design, Phytic Acid.

	Pure PA solution	PA+L	PA+L+Mo
pH 2	#1.2	#2.2	#3.2
pH 4	#1.4	#2.4	#3.4
pH 6	#1.6	#2.6	#3.6

Phytic Acid Combined with Molybdate or Tungstate

The PA solution (50 wt%) was diluted with deionized water to a 5 wt% solution. The pH value of two was adjusted with sodium hydroxide. Potassium nitrate was added as a promoting agent (2 g/L). Sokalan VA 64P was incorporated as a leveling agent (1500 ppm). To achieve better corrosion properties, the inhibitor ammonium heptamolybdate (Mo) or sodium tungstate (W) were used, whereas 10 wt% heptamolybdate or 9 wt% tungstate based on PA content were added to the solution. The concentrations are near the solubility limit of the metal anions. The samples were immersed for six minutes (steel) or three minutes (zinc) in the PA solutions (Table 2). The temperature of the solution was set to 35 °C.

Table 2: Experimental Design, PA Combined with Molybdate or Tungstate.

Substrate	PA+Mo (10 %)	PA+W (9 %)	PA+Mo (10 %)+L	PA+W (9 %)+L
Steel	#4.1	#5.1	#6.1	#7.1
Zinc	#4.2	#5.2	#6.2	#7.2

2.3 Characterization

SEM: The SEM pictures were obtained with a Zeiss DSM 982 Gemini device coupled with an EDX device “Oxford Instruments XMax^N”.

RAIRS: The RAIRS spectra were measured with the Bruker Vector 22; IRRAS-module: Typ A 518 Refl. Unit 80°.

Electrochemical Methods: The EIS spectra and the CV were performed with a Zahner Zennium, Zahner-Elektrik GmbH.

CV: A solution of 3 wt% NaCl in deionized water was used as electrolyte. A scan rate of 100 mV s⁻¹ for non-coated

steel surfaces was used to assure that no iron dissolves into the solution. The PA layers were measured with a scan rate of 20 mV s⁻¹. The upper potential for all measurements was -0.3 V, the lower potential was -1 V and the starting potential was -0.6 V.

EIS: A 3 wt% solution of NaCl in deionized water was used as electrolyte. The amplitude was set to 10 mV. The frequency range was 100 mHz to 100 kHz. Stainless steel served as counter electrode.

SST: The SST were performed in the device from Liebisch Laborgeräte; Constatwin.

Contact Angle: The contact angles from water of the con-

version layers were evaluated with the Device from Data-physic, Contact Angle System OCA 15plus.

3 Results and Discussion

3.1 Estimation of Conversion Layer Thickness

For estimation of conversion layer thickness, the density of iron phytinate was determined to be about 2.34 g/cm^3 . After 30 minutes of immersion time at pH 2, an average thickness of $200 \text{ nm} (\pm 50 \text{ nm})$ was deposited. When leveling agent was added the conversion layer thickness was higher caused by better substrate wetting. Based on the interference colors (blue and red) of the conversion layer (Figure 2), the thickness was between 118 nm and 188 nm , i.e. the same range as the evaluation based on the density of iron phytinate. The rough estimation was based on the wavelength 450 nm for blue and 750 nm for red and the thickness was calculated with the Bragg equation:

$$2dn = (2m + 1) \frac{\lambda}{2} \wedge m = 0, 1, 2, 3, \dots \quad (1)$$

In the equation d is the thickness of the layer, n the refractive index (estimation $n = 1$), λ the wavelength, and m (estimation $m = 0$) the order of the interference.

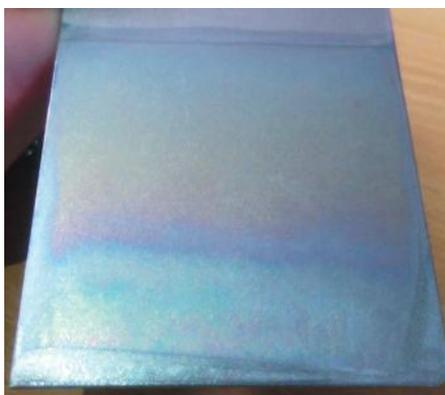


Figure 2: Picture of PA Conversion Layer on Steel.

3.2 Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy

SEM/EDX pictures (Figure 3) illustrate the surface morphology of the conversion layer at different pH values and magnifications. In all SEM pictures, PA could be verified. The element analysis confirmed the following elements: P, O, Fe, C, Na, and K. Phytic acid contains P, O, and C, hence these elements of the analysis can be traced back to the PA. Iron is related to the substrate, while sodium and potassium

is related to the additives. Figure 4 illustrates the element distribution in weight percent. Approximately 6 wt\% of phosphorus and about 20 wt\% oxygen were detected on all metal surfaces. The element ratio phosphorus:oxygen nearly correlates to the structure of PA (6:24).

At different pH values, the covered surface varies. It could be found that the best coverage is at pH 2 and decreases from pH 4 to pH 6. The same behavior is described in literature.^[11] In Figure 3 d, an epitaxial growth could be seen on the PA conversion coating. In general, the morphology of PA showed some cracks. The reason for these cracks is the hydrogen evolution during the treatment process. (Figure 3 e & f).^[3]

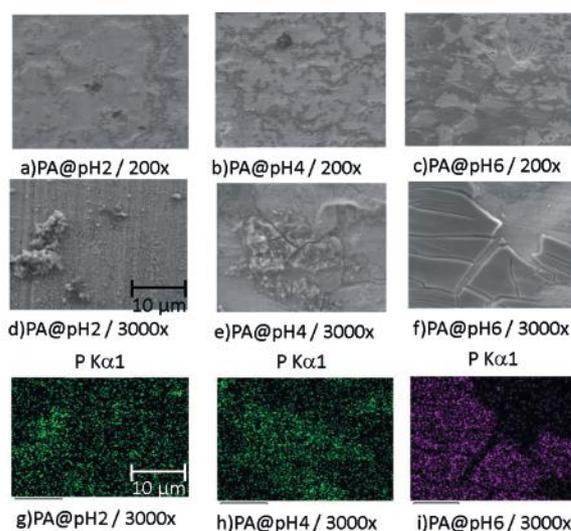


Figure 3: SEM / EDX Spectra of PA Layers on Steel.

To reduce the amount of cracks, a leveling agent was added to the PA solution. The leveling agent improved the wetting and showed a homogenous leveling on the metal surface. Polymer spheres of incompatible leveling agent could be found on the PA surface (Figure 5 d). This effect only exists at pH 2. Especially at the pH level of 6, the surface coverage could be improved compared to the sample without leveling agent (Figure 5 b). With regard to the amount of cracks, no advantage could be achieved. In Figure 5 c, the bright areas represent chipped conversion coating (see EDX picture Figure 5 i). The incorporation of leveling agent boosted the adhesion (Figure 5 b).

In further experiments, molybdate anions were additionally added to the leveling agent (Table 1). With this inhibitor, an extra benefit for corrosion performance should be achieved. The EDX picture (Figure 5 i) shows that molybdate was homogeneously distributed in the PA conversion coating. The amount of cracks was lowered with the combination of corrosion inhibitor and leveling agent (Figure 5 f). One explanation of this observation is the high coordination to other elements and therefore higher network density of molybdenum compounds.

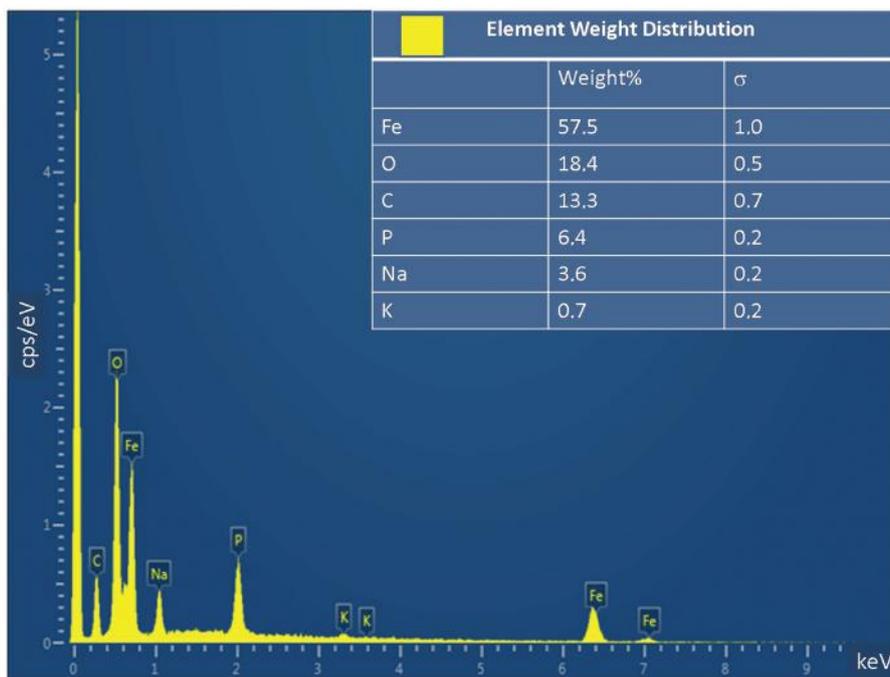


Figure 4: Element Weight Distribution #1.2 (Table 1).

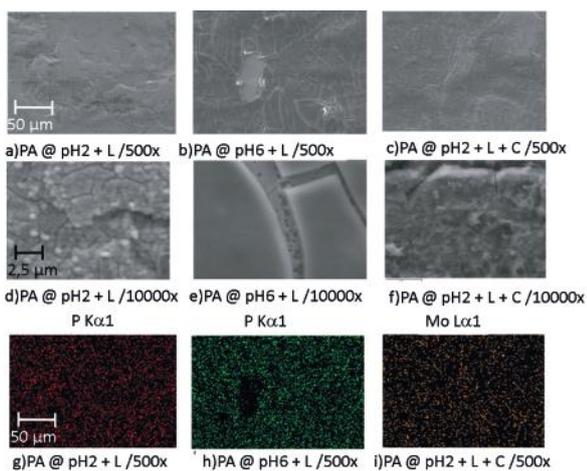


Figure 5: SEM / EDX Spectra of PA Conversion. Coating with Modifications (L: Leveling Agent, C: Corrosion Inhibitor).

3.3 Infrared Spectroscopy

The RAIRS spectra of PA and their conversion coatings at different pH values are displayed in Figure 6. The spectrum of PA and conversion coatings showed three bands at 972, 1011, and 1047 cm^{-1} , assigned to the P–O–H bond. Only for the PA spectrum, three bands at 951, 827, 737 cm^{-1} ($-\text{PO}_4^{3-}$) could be seen.^[3] The bands at 1375 (PA) and 1371 cm^{-1} (PA conversion coating) were assigned to the $-\text{P}=\text{O}$ bond.^[12] The bands around 1600 cm^{-1} were related to HPO_4^{2-} groups.^[3] For the conversion coating, it is obvious that the phosphate hydrogen group was present while the phosphate group was absent. This indicates that the phosphate group of PA can form complexes with metal ions such

as Fe^{2+} and Fe^{3+} resulting in the conversion coating on mild steel. The bands in the spectra of the conversion coating below 700 cm^{-1} also support the theory of the formation of metal-oxygen bonds.^[12] It proved that PA was deposited on the metal surface. The samples of different pH values were similar to each other. Only in the range of 3500 cm^{-1} , the bands show differences. At pH 6, the band for $-\text{OH}$ is more intensive than at pH 2 and 4. The reason for this is a lower deprotonation at pH 6.

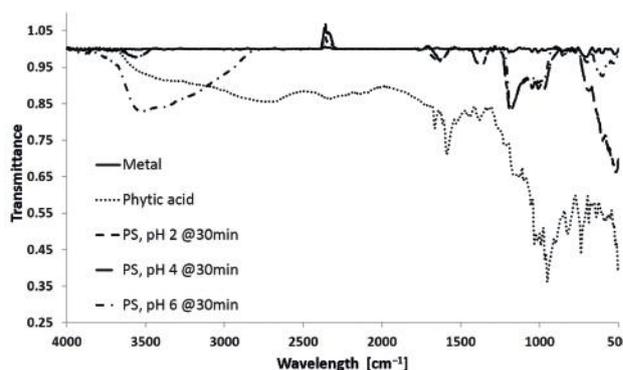


Figure 6: SEM / EDX Spectra of PA Conversion. Coating with Modifications (L: Leveling Agent, C: Corrosion Inhibitor).

3.4 Cyclic Voltammetry

The cyclic voltammetry was used to determine the surface coverage of the PA layers on steel in contrast to non-coated mild steel.^[13] With respect to the different scan rates, it was assumed that the charge transferred with the faster scan rates of the uncoated iron equals one fifth of the charge

transferred of the steel covered with PA.

$$5 \cdot t_{Fe} = t_{Phyt} \text{ and } Q = I \cdot t \rightarrow 5 \cdot Q_{Fe} = Q_{Phyt} \quad (2)$$

$$\Theta = 1 - \frac{Q_{Phyt}/A_{Phyt}}{5 \cdot Q_{Fe}/A_{Fe}} \quad (3)$$

The coverage increased after incorporation of the leveling agent. The highest coverage of 74 % could be reached using the leveling agent and corrosion inhibitor (Table 4). This is explained by the better surface wetting resulting in smoother surface coverage using the leveling agent as discovered in the SEM measurements (Figure 5 f).

Table 3: Cyclic Voltammetry Results.

Sample	Area / cm ²	Charge / mC	Charge/Area / mC/cm ²
mild steel #1	1.68	4.88	2.90
mild steel #2	2.38	2.83	1.19
mild steel #3	2.24	3.35	1.50
mild steel #4	2.08	2.33	1.12
		mean x 5	8.39

Table 4: Surface Coverage.

Sample	Area / cm ²	Charge / mC	Charge/Area / mC/cm ²	Coverage / %
#1.2	1.3	4.5	3.5	58.5
#2.2 - 1	2.1	6.2	2.9	65.0
#2.2 - 2	2.2	6.5	2.9	65.6
#3.2 - 1	2.3	5.0	2.1	75.1
#3.2 - 2	2.2	5.0	2.2	73.3

3.5 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy was used to determine the corrosion behavior of PA coated steel. Figure 7 shows the impedance spectrum of a steel surface coated with PA at pH 2 at different times. The measurements showed a rapid dissolution of the PA layer (Figure 7) because the conversion layer was represented by a semicircle in the spectra that was only visible at $t = 0$ min.

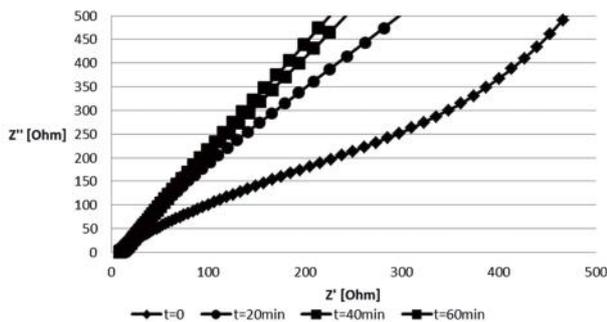


Figure 7: Nyquist plot of the Conversion Layer Deposited at pH = 2 on Steel at Different Times.

The half circle demonstrates a PA coating on the substrate.^[14] With corrosion inhibitor (L+C), two half circles indicated the existence of a layer and an electrochemical double layer at the interface. Only the phosphated steel showed an active dissipation (Warburg impedance) visible by a linear behavior at low frequencies.^[14] After 25 min-

utes, phosphate steel has the same behavior but the PA coatings vanished (Figure 8).

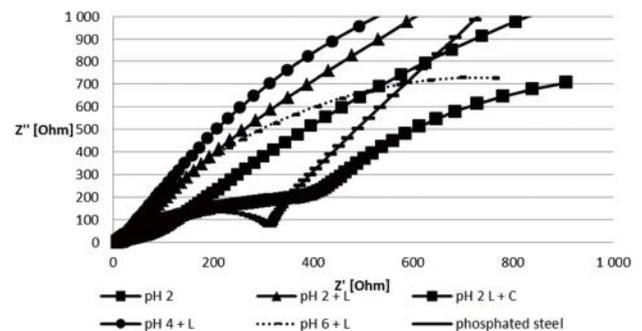


Figure 8: Nyquist-Plot at the Beginning ($t = 0$ min) of the Measurement.

3.6 Salt Spray Test

PA Layer

To determine the corrosion of the samples, a neutral SST was done. The samples were sprayed with a 2 pac acrylate clear coat (cross linking agent: isocyanate). All samples had a dry film thickness of $35 \pm 5 \mu\text{m}$. The test duration was 68 hours. The degree of delamination was observed according to DIN EN ISO 4628-8 (Table 5).

Overall, PA conversion coatings did not show the same performance as phosphate steel. At least modification with molybdate (Table 1, #3.2) showed a better resistance against delamination as the pure PA conversion layer.

Table 5: Delamination after 68 h SST.

Sample	d / mm
Phosphated steel	0.5
#1.2	11
#2.2	15
#3.2	8
#1.4	18
#1.6	20

Phytic Acid Combined with Molybdate or Tungstate

To determine the corrosion of the samples a neutral SST was done. The samples were sprayed with a 2 pac epoxy based marine coating (cross linking agent: amine). All samples had a dry film thickness of $100 \pm 10 \mu\text{m}$. Two samples of every layer system have been tested in the SST. The test duration was 215 hours. The degree of blister formation was observed according to DIN EN ISO 4628-8 (Table 6).

Table 6: Blister Formation After 215 h SST. The Values are the Average of Two Samples.

Sample	Blister Size / Amount
Blind sample zinc	2/3
Blind samples steel	2/4
Blind samples phosphated zinc coated steel	1/3
#4.1	2/5
#4.2	1/3.5
#5.2	2/2
#6.2	1.5/3.5
#7.1	2/5

The missing samples in Table 6 have not been tested because no film formation of phytic acid with tungstate was possible under the conditions. Regarding the blister formation, the conversion layer #4.2 based on PA and molybdate achieved the performance level of the phosphate surface. The evaluation of the delamination rate after 215 hours gives a clear picture (Figure 9) about the performance of PA based conversion layers. All samples based on PA conversion layers completely delaminated and corrosion was visible on the complete sample surface.

There might be a protective effect of the conversion layer but there is no wet adhesion to the epoxy based coating. The same effect is visible on the 2 pac acrylate clear coat.



Figure 9: Pictures of the Treated Samples After 215 Hours SST. Left to Right: Steel, Phosphate Steel, Zinc, PA/Molybdate/Leveling Agent on Steel, PA/Molybdate on Zinc, and PA/Tungstate on Zinc.

4 Conclusion

The results show that it is possible to deposit PA as a conversion coating. The formation and morphology of the coating depends on the pH value and the concentration of metal ions in the solution. It could be proved by IR and SEM/EDX that PA is precipitated. Furthermore, the leveling agent leads to the advantages of better wetting, higher coverage, and film thickness. Nevertheless, the conversion layer cannot improve the corrosion protective properties of an organic coating as shown with a 2 pac acrylate based clear coat and with a 2 pac epoxy based marine coating. The reason for this behavior probably originated from the low contact angle of the PA based conversion layer to water (Figure 10) and therefore a good wettability of the interface between conversion layer and coating. The wet interface reduces the adhesion between the coating systems, whereas the corrosion protective properties were completely destroyed.

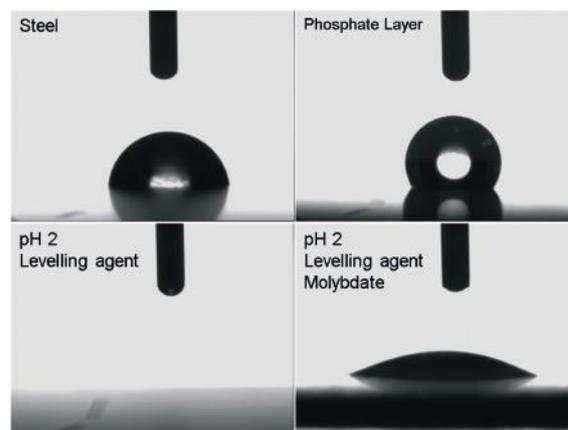


Figure 10: Pictures of the Contact Angle Measurement of the Surfaces with Water.

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