

HTT 1800 SILAZANE AS HIGH PERFORMANCE COATING TO STAINLESS STEEL SUBSTRATE

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ABSTRACT - Stainless steel has been used for years as a commodity in the most different fields of industry due to its excellent physical and chemical resistance properties, however highly undesired energy expenditure on the forced abrasion of fluids to the steel wall is caused due the material's rough surface and friction. Silazane polymer-derived ceramic coatings may be a promising alternative to this problem by modifying the substrate surface and wettability. Thereafter, AISI 304 steel samples were dip-coated in HTT 1800 solutions and treated thermally at temperatures ranging from 200-700 °C in order to evaluate the coating thermal resistance and interaction to different liquids. Fillers were also as to tailor greatly the interaction with liquids at high temperatures (400-500 °C). In comparison to the raw substrate, the coated samples exhibited a more oleophobic and more hydrophilic behavior. TGA analysis detected a mass loss of about only 20% for the pure coating material at 1000 °C.

1. INTRODUCTION

Stainless steel has been widely used thorough the years on the most various metal structures in chemical, civil and mechanical industry fields due to its good physical and chemical properties. However, the energy expenditures related to the pumping of viscous fluids through pipelines and the constant abrasion to the steel wall in mixing vessels, reactors due friction represents a major drawback to be dealt with. In addition, failure due to corrosion and fatigue is very common and threatens the equipment lifetime span.

Modified surfaces have an extensive range of applications relying on the surface level of interaction to different liquids. These functionalities comprise of self-cleaning properties, fluidic drag reduction, anti-fouling, enhancing of water supporting forces on floating objects, water corrosion resistance and others (Zhang *et al.*, 2007), hence turning it into a suitable candidate to overcome the drawbacks presented above. The level of interaction to different liquids is commonly described by the contact angle formed by a droplet in contact with a surface.

The disparity between the cohesive and adhesive forces in the liquid, which tend to bring it together as a droplet or spread it on the surface define the equilibrium contact angle. It is directly related to the surface's free energy or tension, and a simple tension balance derivation leads to a very useful relationship regarding the contact angle formed, first described by Young (Adamson & Gast, 1997). Later Wenzel and Cassie-Baxter developed

new models reporting the droplet behavior on a surface. These models cannot prove to be superior one to another, but can only complement the phenomenon description. They consider not only the liquid and vapor's surface and interfacial tension but also the solid surface roughness in order to determine its wettability (Liu *et al.*, 2013).

A liquid is said not to wet a surface when the contact angle is greater than 90° , thus the surface is classified as hydrophobic or oleophobic. On the other hand, a liquid is said to wet a surface when the contact angle is 0° (Adamson & Gast, 1997). In extreme cases, the surface can still be classified as superhydrophobic or superoleophobic when the contact angle is greater than 150° (Burkarter, 2010).

Inorganic precursor based coatings act as a barrier and offer protection against corrosion and abrasion to the coated material even at high temperatures (Günthner *et al.*, 2009) promptly modifying the substrate surface, possibly favoring this study's main concern towards friction and corrosion.

Coatings such as those derived from silicon inorganic precursors are mainly covering layers as polysiloxanes, polycarbosilanes. Moreover, these inorganic covering layers can undergo a pyrolysis process where polymer-derived ceramics (PDC's) are formed (Günthner *et al.*, 2009; Seyferth, 1990) and, depending on the applied atmosphere on the pyrolysis process, the growth of an SiO_2 layer can be observed (Günthner *et al.*, 2009), which accounts for an exceptional performance of these PDC's coatings in oxidative environments, once it presents one of the lowest oxygen permeability among the simple oxides (Nickel, 1999; Chollon, 2000; An *et al.*, 2004).

In order to tailor the coating properties, fillers can also be added to the pre-ceramic polymers. Depending on the filler nature, it can be responsible for a set of changes in the coating, including an increase on the critical thickness (maximum thickness value before cracks start appearing), special friction properties, higher chemical stability, superior adhesion, catalytic activity and others (Colombo *et al.*, 2009; Majumdar *et al.*, 2001).

This work focuses on the manufacture of HTT 1800 polysilazane coatings for AISI 304 stainless steel substrate with the goal of modifying the level of interaction between the steel and different liquids to avoid fouling and improve flow properties specially at higher temperatures ($> 300^\circ\text{C}$) and as a consequence, increase the material's resistance to corrosion and fatigue.

2. EXPERIMENTAL PROCEDURE

The steel substrate consisted of AISI 304 stainless steel samples sized 1.5 mm thickness, 30 mm width and 60 mm length as it represents the manufacturing material of the equipments of interest to be coated.

The materials selected for the coating preparation were KiON HTT 1800 to act as the main coating material, supplied by AZ Eletronic Materials, Wiesbaden, Germany, dicumyl peroxide (DCP) to act as a cross-linking agent, supplied by Sigma-Aldrich Chemie GmbH, Steinheim, Germany and di-n-butylether as the medium solvent, supplied by Alfa Aesar

GmbH & Co KG, Karlsruhe, Germany. The fillers selected for this work were SiO₂ Aerosil R812S D₅₀ = 0.90 μm provided by Degussa AG, Frankfurt am Main, Germany and Al₂O₃ Aeroxide Alu C805 D₅₀ = 0.75 μm, provided by Degussa AG, Düsseldorf, Germany.

In the first part of the work, a solution of 50 wt% of HTT 1800 + 3 wt% DCP as coating material and 50 wt% di-n-butyl ether as solvent was prepared where the AISI 304 steel samples were dip-coated at a controlled speed of 0.1 m.min⁻¹ in a dip-coater model Relamatic RDC 15, Glattbrugg, Switzerland to guarantee that a homogeneous HTT 1800 + 3 wt% DCP coating would be obtained and to achieve the necessary thickness and avoid cracks on the coating surface. The samples were then treated thermally in a controlled air atmosphere at a heating rate of 3 K.min⁻¹ where the temperature was kept still for 1 hour after it had been reached. The applied treating temperatures were in a range of 200 to 700 °C on 100 °C gaps in order to evaluate the coating response to temperature. The samples were thermally treated in an oven model Nabertherm B 150, Nabertherm GmbH, Lilienthal, Germany.

Distilled water was chosen to evaluate the coating response to hydrophobicity in contact angle analysis in a 250-F1 Ramé-Hart Inst. Co., Succasunna, New Jersey, USA goniometer while the coating oleophobicity was tested through dripping two highly non-polar liquids, n-hexadecane 98% P.A., supplied by Vetec Química Fina Ltda., Rio de Janeiro, Rio de Janeiro, Brazil and petroleum Merluza, donated by Petrobras S.A., Brazil through the same contact angle analysis. The contact angle was measured a few seconds after the droplet stabilized. Each analysis was run in triplicate and the mean contact angle average and standard deviation were calculated.

The second step consisted of focusing the analysis on higher treating temperatures of 400 and 500 °C, which is the coating desired temperature of work and the temperature which the material starts to fragilize at long exposures according to the North American Stainless (NAS) catalog for Long Products Stainless Steel Grade Sheet, AISI 304-304L, 2010. The coatings were filled with SiO₂ and Al₂O₃ as follows on table 1.

Table 1 - SiO₂ and Al₂O₃ filled coatings description

Code	di-n-Butyl ether (wt%)	HTT 1800 (wt%)	SiO ₂ (wt%)
P01	98%	0.5%	1.5%
P02	98%	0.7%	1.3%
P03	98%	1.0%	1.0%
	di-n-Butyl ether (wt%)	HTT 1800 (wt%)	Al ₂ O ₃ (wt%)
P04	98%	0.5%	1.5%
P05	98%	0.7%	1.3%
P06	98%	1.0%	1.0%

To those solutions on Table 1, a total of 5 wt% DISPERBYK 2070, BYK-Chemie GmbH, Wesel, Germany dispersing agent was added regarding the total amount of filler added, independently of the other quantities in the solution. The samples were characterized through the same procedure mentioned above for the first part of the work, also in triplicate.

The HTT 1800 + 3 wt% DCP thermal stability was measured via thermogravimetric analysis (TGA) model Linseis A1550, Linseis Messgeräte GmbH, Selb, Germany at a heating rate of 3 K.min⁻¹ up to 1000 °C as the total mass loss was calculated.

3. RESULTS AND DISCUSSION

3.1 Contact Angle Analysis

Table 2 exhibits the contact angle analysis results of uncoated AISI 304 stainless steel samples treated at 500 °C (Table 2.2) and not treated thermally (Table 2.1) as a matter of comparison to the coated samples.

Table 2. Uncoated AISI 304 steel samples dripped with different liquids

Table 2.1 - Uncoated steel not treated thermally		
Liquid	Mean Contact Angle (°)	Standard Deviation (°)
Distilled Water	91.60	0.35
N-hexadecane	0.00	0.00
Petroleum	0.00	0.00

Table 2.2 - Uncoated steel treated at 500 °C		
Liquid	Mean Contact Angle (°)	Standard Deviation (°)
Distilled Water	83.58	5.78
N-hexadecane	0.00	0.00
Petroleum	0.00	0.00

Tables 3 and 4 refer to the first part of the work, where distilled water, n-hexadecane and petroleum Merluza were dripped on the coated steel surface at a range of temperature of 200 to 700 °C and the contact angles were measured.

Table 3 - HTT 1800 + 3 wt% DCP coated steel samples dripped with distilled water

Distilled water		
T (°C)	Contact Angle (°)	Standard Deviation (°)
200	94.60	2.76
300	79.40	2.74
400	60.37	4.45
500	55.00	1.56

600	62.90	1.47
700	65.47	4.17

Table 4 - HTT 1800 + 3 wt% DCP coated steel samples dripped with n-hexadecane and petroleum Merluza

T (°C)	N-hexadecane		Petroleum Merluza	
	Contact Angle (°)	Standard Deviation (°)	Contact Angle (°)	Standard Deviation (°)
200	34.65	0.91	0.00	0.00
300	17.90	2.23	0.00	0.00
400	15.35	4.31	0.00	0.00
500	0.00	0.00	0.00	0.00
600	0.00	0.00	0.00	0.00
700	0.00	0.00	0.00	0.00

From the results on Tables 2.1 and 2.2, n-hexadecane and petroleum Merluza are said to wet the surface, as the contact angle measured is 0° and therefore, the AISI 304 uncoated steel samples are classified as oleophilic. The spreading phenomenon observed on the samples tested above can probably be related to the low surface tension of the n-hexadecane and petroleum liquids, which are closely two thirds lower than water's. (**Surface tension values of some common test liquids for surface energy analysis**, available at <http://www.surface-tension.de/>, accessed on February 18th, 2014 at 15:22.54).

As expected from above regarding the surface tension, the water droplet maintained a more rounded shape as the mean contact angle increased. Thus, the samples on Table 2 are in the limit zone for hydrophobicity. If the contact angle is greater than 90°, the drops of liquids tend to move freely on the surface, not entering the capillary pores. Moreover, if the contact angle is large (i.e. approximately > 90°) and the surface is sufficiently rough, the liquid may trap air so as to give a composite surface effect increasing the real contact angle (Adamson & Gast, 1997).

For the runs with distilled water, the sample can be classified as slightly hydrophobic although the thermal treatment reduced the contact angle classifying the sample on Table 2.2 as hydrophilic.

From table 3, the coated samples became more hydrophilic as the curing temperature increased. Samples cured above 200 °C can be classified as hydrophilic, as the mean contact angle remained below the value of 90°, excepting the curing temperature of 200 °C, which could be classified as slightly hydrophobic, as the mean contact angle is only slightly above 90°.

The samples on table 4, dripped with n-hexadecane, have shown to be very oleophilic-oriented, as the mean contact angle of all samples remained below 90 °C. It can also be

withdrawn from the results that as the curing temperature increased, the oleophilic interaction strengthened and the contact angle approached 0°.

For samples dripped with petroleum on table 4, their behavior approached greatly the superoleophilicity, as the contact angle also approached 0°.

Further tests were conducted with HTT 1800 filled material. The coatings description and analysis results are available below.

Table 5 - Mean contact angle for HTT 1800 filled samples dripped with distilled water

Sample	T (°C)	Contact Angle (°)	Standard Deviation (°)
P01	400	136.48	1.63
	500	14.67	4.82
P02	400	141.48	1.77
	500	15.08	1.80
P03	400	137.13	7.04
	500	14.83	5.24
P04	400	49.72	3.85
	500	43.85	2.62
P05	400	44.52	5.62
	500	51.80	1.74
P06	400	88.22	1.98
	500	57.20	4.07

Each sample was tested at least three times and the mean width, height and contact angle values for distilled water are shown on table 5. The results for n-hexadecane and petroleum for the samples coated with HTT 1800, di-n-butylether and SiO₂ or Al₂O₃ were not listed since it approached 0°, confirmed by the total spreading of the drop once it touched the material surface.

The samples filled with SiO₂ cured at 400 °C are very promising hydrophobic coatings as the contact angle remained high above 90°. On the other hand, the samples coated with HTT 1800 and filled with Al₂O₃ were only classified as hydrophilic due to the low contact angles observed on table 6.

An increase on the curing temperature of 100 °C for the samples filled with SiO₂ appears to have significantly affected the coating behavior, turning it into hydrophilic and strengthening its interaction to polar liquids.

Although the same temperatures were applied to curing the samples filled with Al₂O₃, the coating behaved differently in order to strengthen the polar affinity to liquids on samples

P06 and P04 and as to decrease it on sample code P05 as the temperature ranged from 400 to 500 °C.

3.2 Thermogravimetric Analysis

Thermogravimetric analysis was performed at a heating rate of 3 K.min⁻¹ up to 1000 °C in air atmosphere. The residual mass loss and the HTT 1800[®] thermal stability were evaluated accordingly to the results.

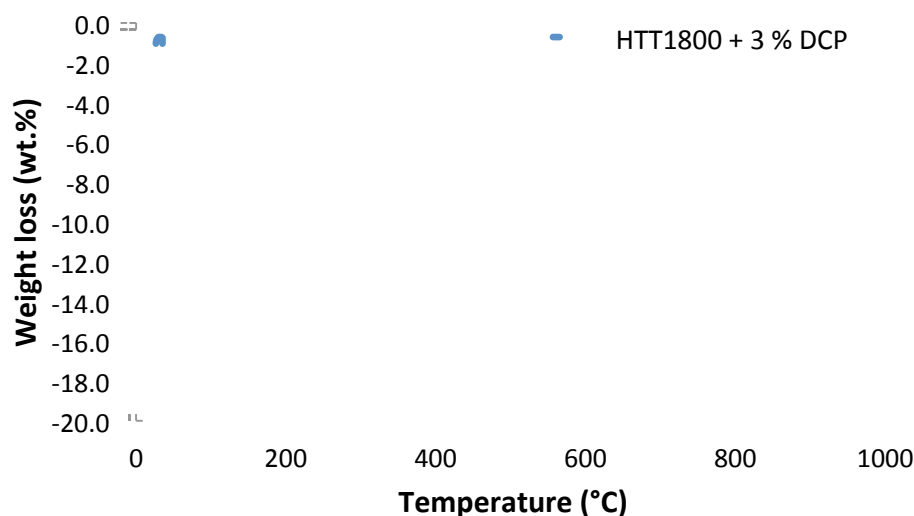


Figure 1 - Pure HTT 1800[®]/3 wt.% Dicumyl Peroxide TGA curve

The TGA curve confirms the thermal behavior expected for the ceramic material, as the mass change remained slightly above -20 wt.% at a temperature of approximately 1000 °C. This stability is mainly due to the covalent Si-X bonds (X = C, H, O or N) bonds present in the chemical compound backbone, which need about an average of 90 Kcal to be dissociated (Common bond energies available at http://www.wiredchemist.com/chemistry/data/bond_energies_lengths.html accessed on June 30th, 2014 at 23:38:30). The thermal stability could also be related to the ceramic yield at high temperatures, preventing further mass loss.

4. CONCLUSION

The surface tension analysis revealed how polar and non-polar liquids interact with uncoated AISI 304 steel and HTT 1800 coated samples.

Uncoated AISI 304 steel tends to be hydrophobic when in contact with polar liquids, such as water. Non-polar liquids such as n-hexadecane and petroleum, showed a contact angle lower than 90° in contact with uncoated AISI 304 steel and the surface was therefore classified as oleophilic.

The AISI 304 steel coated with HTT 1800 100 wt.% samples revealed to be mostly oleophilic and hydrophilic, as the contact angle of almost all runs remained below 90°. The only exception was the HTT 1800 coated sample, cured at 200 °C, which exhibited a hydrophobic behavior. As the curing temperature rose, the interaction between liquids and coating intensified and the contact angle lowered.

The coatings filled with SiO₂ or Al₂O₃ behaved similarly to the samples above, although a temperature range of 100 °C in the curing of the same samples altered significantly the coating behavior and strengthened its interaction with polar liquids for SiO₂. The same range for Al₂O₃ filled samples did not change much the contact angles in the final results.

SiO₂ filled samples cured at 400 °C are a better alternative to hydrophobic coatings as the mean contact angle remained highly above 90°, unlike any other coating in this work, which favors the pumping of viscous polar liquids through surfaces coated by this material.

As a final closure, the material is also very suitable at high temperatures application as shown by the TGA curve. The residual mass remained slightly above 80 wt.%.

5. REFERENCES

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