THE STAINLESS STEEL TEST SURFACE

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INTRODUCTION

The objective of this paper is to present the findings from an investigation into why peel adhesion values seem to change when testing PSA products on different lots of stainless steel test panels. The shift in data is mostly reported when a laboratory purchases new test panels and the new data does not fall within specification limits or the historical trend of data produced with older test panels. To begin the investigation, three potential contributing causes were investigated; 1) the stainless steel content and manufacturing conditions, 2) surface roughness tolerances and 3) cleaning procedures and solvent chemicals.

Stainless steel is manufactured at steel mills around the world. One might think that 304 stainless steel (SS) is the same everywhere. However, it was discovered during this investigation that formulations can change from mill to mill and still be within the 304 specification. Other differences were discovered in the annealing conditions.

The bright annealing process generally produces a surface roughness of 2 ± 1 micron. This has been the standard for bright annealed stainless steel as a test surfaces established in the 1950's. A key question focused around a peel adhesion test and the difference between a 1.5 and 2.0 µinch median surface roughness. It is possible to use a standard surface as a starting point and then add an additional buffing process to create a smoother surface. Rather than a mill finish of 2±1micron, a buffed panel can be 1.5±0.5 micron target. Herein, these two surface roughness findings will be disclosed.

The test panel cleaning process allows a test panel to be reused and is the last process prior to performance of the test. Test panel cleaning also provides the most opportunity for variation. The PSTC Appendix C for cleaning test surfaces lists a choice of several solvents which are thought to remove most adhesive residue. In discussing alternate cleaning methods with several different companies, it has been found that many followed very different cleaning methods which can range from ultrasonic water bath to a long chemical soak.

BACKGROUND

What are some of the issues that prompted this study? Why do I see a shift in my peel adhesion results when I use a new lot of test panels? Why do I see peel adhesion results change over time?

A question which appears in many labs is, "how reliable is our peel adhesion data?" Are the specifications set too close for the error which could be present in the test? The problem could lie in a shift in data over time with continued use of old panels, with a new lot of panels, or with what seemed like a minor change in a material prompted a significant shift in data. Could one technician clean more or less diligently than another? There are several solvents called out in panel cleaning recommendations, but are we using the correct solvent for our adhesive? The answer to all of these is, “it depends”. With the vast array of adhesive technologies and formulations within those technologies, there is no single response to any of these questions.

How are the stainless steel manufacturing variables controlled? First we need to understand the process for producing SS test panels. Most 304 bright annealed stainless sheeting is supplied to manufactures for industrial holding tanks, or restaurant counter tops and cookware. The steel mills can produce different formulations of stainless steel and while they work toward a Bright Annealed (BA) specification to generate a certain smoothness, there are variations from mill to mill and process to process.

The steel mill does not consider how their process buffer oils and protective covers contaminate the surface before the cut panel even arrives at our lab. There is no standard written to inform the steel manufacturing plant about the quality of the nitrogen blanket used at annealing or specific buffers or protective covers which should be used to prepare the finish to be used as a test surface. Our industry’s use of stainless steel is not of the volume to control or influence the steel manufacturers. Therefore, an initial cleaning to decontaminate the surface is essential.

1) For new test panels, current recommendations in PSTC’s test methods advises to bake panel after removing the protective cover when the panels are first received. This step will help eliminate residual process oils, plasticizers or other contaminants that may be present. Then it is recommended to follow this baking step with a solvent wash.
2) In repeat use, the current recommendations in PSTC’s test methods suggest a series of solvent washes to be used after or between each panel use. The number of washings is also recommended to be thorough.

Various tests are used in the PSA industry to characterize performance and consistency. The most prevalent tests are peel adhesion, tack and shear. All of these tests are typically conducted on a standard stainless steel panel having a bright annealed finish with a defined surface roughness. While obvious surface defects such as scratches will affect the results, one very important aspect is cleanliness or elimination of surface contaminants before each test. The use of clean panels is relevant to all adhesive testing.

Experimental

This study used the 180° peel test to examine the effect of variables. The peel test provides a good look at a large surface area as opposed to a loop tack test which also factors in the rigidity of the backing. A shear test is intended to split the adhesive layer and it does not give an indication of the adhesive interaction at the panel surface. The peel test is dependent on the interaction at the surface of a “clean” stainless steel panel and the adhesive product under examination. A peel adhesion also allows for a variable of dwell time to look at the surface interaction over time with different types of PSA’s.

The first and most direct parameter which was investigated was the surface roughness. For this experiment, two roughness levels were used and both are within the PSTC allowable range. The first set is a standard panel with a surface roughness of 2.0 micron. The second set was made from the same lot of panels (same stainless composition) and an extra buffing process was added to create a surface roughness of 1.2 micron. These panels were solvent washed with MEK or Acetone, baked 175 °C for 1 hour, and rewashed with the same solvent prior to testing. An acrylic masking tape was applied to the panels with a 2 Kg roller, after a 1 minute dwell the adhesive was removed at 300 mm/minute.

Table 1. Surface Roughness Comparison

Surface Roughness				
180° Peel Adhesion, Acrylic Adhesive, **N/10 mm**				
	1.2 µ		2.0 µ	
Replicate	MEK	Acetone	MEK	Acetone
1	1.58	1.73	1.57	1.55
2	1.72	1.65	1.76	1.70
3	1.82	1.77	1.85	1.65
4	1.80	1.66	1.80	1.57
5	1.74	1.75	1.85	1.67
AVG	**1.73**	**1.71**	**1.77**	**1.63**
St. Dev.	0.09	0.05	0.12	0.07

When the first column (1.2 micron) was compared to the second column on the right (2.0 micron) with a Student's t-test, there were no indications that any of the results were significantly different from the other (Table 1). The limited testing showed no affect due to surface roughness and both panel groups were within the excepted range for standard test panels. With no essential differences found in surface roughness, the testing for this paper would be performed with standard roughness panels averaging 2.0 micron.

The focus then moved to preparing new panels for use. As mentioned above, the PSA industry does not drive stainless steel manufacturing, each lab must prepare panels for initial use by removing a variety of manufacturing contaminates**.**

Following the current recommendations in PSTC for new panel preparation**,** twenty panels were MEK washed, baked at 175°C (350°F) for 1 hour then MEK solvent wiped again to remove residual contamination. This initial wash and baking will help eliminate residual process oils, plasticizers or other impurities which may be lingering on the surface after removal of the protective cover.

Each solvent on the suggested list was used to determine if any one of these solvents should be recommended as the initial solvent for new panels. A series of peel adhesion tests followed. Using 5 panels for each solvent, a series of 10 peels were performed with each panel to have a total of 50 replicates to draw the averages in the table. The ten peel series was an attempt to mimic the "break in" time frame. The data for each solvent did not trend consistently up or down throughout the series (Table 2). The 50 tests showed any solvent will perform the new panel cleaning satisfactorily. To challenge this idea, another solvent wash with MEK without the baking treatment was performed. This is not a method recommended in current practices. It was found that MEK without baking produced results in a similar peel range.

Table 2. New Panel Solvent Cleaning

Condition	Baked /PSTC Appen C	
Units: Solvent	N/10 cm	Lb force/inch
Methyl Alcohol	1.56 ±.018	0.86 ±.020
Methyl Ethyl Ketone - MEK	1.45 ±.025	0.80 ±.013
Acetone	1.63 ±.037	.90 ±.015
n-Heptane	1.69 ±.069	.93 ±.015
NO BAKE		
MEK	1.49 ±.044	0.82 ±.024

Data from this test indicates no significant difference between these chemicals.

After this work, it was decided to go back and look at the change which has taken place from removal of the cover to after the first series of solvent washes. One way to check the surface is to measure surface energy. Surface energy can be determined by measuring the contact angle with a droplet of water. Higher surface energy will cause the droplet to spread allowing for good wet out and low surface energy will cause the droplet to bead up. A low surface energy would indicate impurities on the surface. Surface energy will make a difference in the ability of a PSA to wet out the surface and adhere or bond to the steel surface. The first step was to look at new panels which had followed the baking / solvent washing process and found that not much had changed and contact angle was higher than expected. Higher contact angle indicates a lower surface energy.

Naturally, steel should have a high surface energy and the droplet should have a very low contact angle. When the cover is first removed the droplet beads up; these angle measurements were typically in the 75-95° range (Figures 1 and 2). The evidence of manufacturing surface contaminants or migration from the protective cover could now be measured in a more direct way, rather than performing a peel adhesion test.

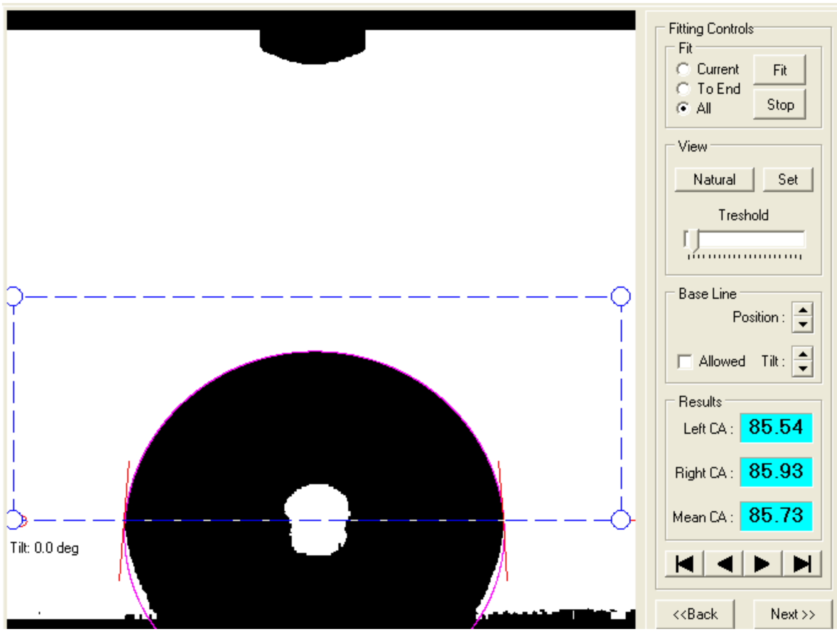

Figure 1. Contact Angle on untreated stainless

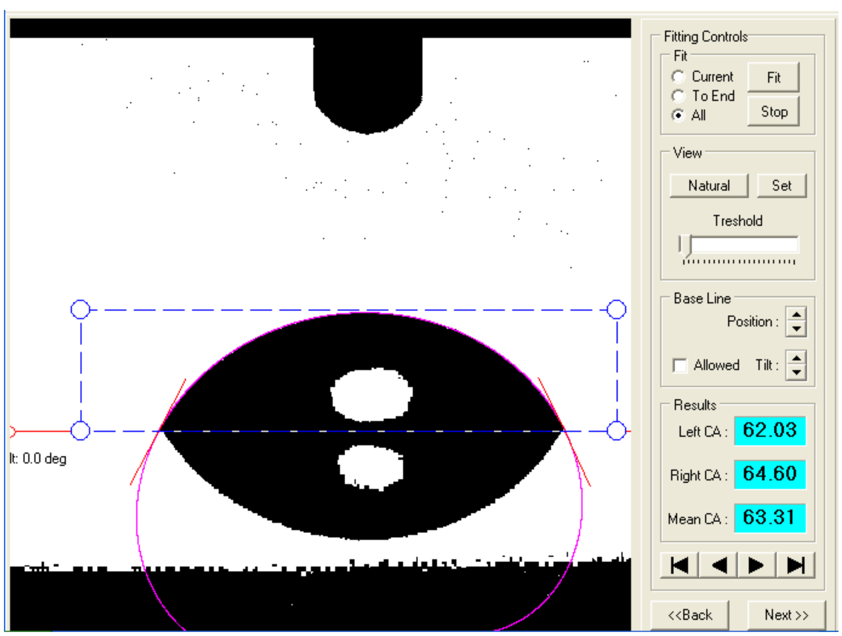

Figure 2. Contact Angle on MEK cleaned stainless

The MEK cleaning used one wash with MEK followed by heat treating at 175°C for 1 hour then four washes with MEK. The contact angle did decrease showing some of the impurities had been removed.

Using only deionized water for this work, it was found that the contact angle scale measures most accurately down to a 20° angle. There are standard contact angle methods for metals which involve the use of other chemicals which were not used in this study. Only deionized water was used on the surface. Three new sets of five panels were measured for contact angle with the cover removed. Initial contact angle testing showed some variation on near neighbor readings for this reason, five sites on each panel were tested to draw an average for each panel.

Five droplets per panel were averaged for the value shown in Table 2. The reading was captured at about 5 seconds after contact. Group 1 and Group 2 had not been assigned a cleaning method at this point. The contact angle was measured as a starting point for the surface energy or wettability.

Table 2. New panel contact angle

Contact Angle			
5 µl, <5 seconds, at ***Cover Removal*** , CA(°)			
	Group 1	Group 2	MEK
1	79	86	92
2	76	87	91
3	78	82	88
4	84	83	85
5	83	88	86
AVG	**80**	**85**	**88**

While there appears to be some variation in the readings, the average values are in the same range. It was agreed that the angle could increase or decrease depending on the next cleaning step applied to the panel. Current recommendations are that MEK should be the last solvent prior to testing; it was decided that this solvent would be included in the study and Group 3 was immediately identified as MEK.

Single panels were cleaned with MEK, Methanol, Acetone and n-Heptane. This was an attempt to find the one or two solvents which reduced the contact angle. The following table shows the results of one panel cleaned 4 times with the single solvent in an attempt to remove manufacturing impurities.

Table 3. Contact Angle after solvent wash

Contact Angle						
5 µl, <5 seconds, **Bake 1 hour then 4 x *Wash***, CA(°)						
Solvent	Site 1	Site 2	Site 3	Site 4	Site 5	**AVERAGE**
MEK	66	63	70	72	65	**67**
Methyl Alcohol	67	74	80	71	84	**75**
Acetone	72	78	74	69	66	**72**
n-Heptane	70	65	73	76	73	**71**
Toluene	62	70	59	71	67	**66**
DI Water Sonicated	55	62	65	66	71	**64**
Contrex	27	29	23	30	34	**29**
Alconox	33	24	29	29	23	**28**

Based on the results shown in Table 3, the suggested solvents did not show much of a reduction in contact angle (above the dotted line in Table 3), other methods and solvents were explored. Keep in mind at this point, this was just a range finding mission to determine if there was a cleaner to bring the surface energy into the expected range of stainless steel. With these alternate cleaners (below the dotted line in Table 3), it appeared that the lab ware cleaners did something to remove the manufacturing impurities and change the contact angle in a positive direction.

The results were significant; the contact angle was raised from a minimum average angle of 80° to an angle of less than 30°. The lower contact angle is associated with more wetting of the water droplet.

With this method, a clear look at how contact angle relates to peel adhesion could be performed. In the beginning of the study there were two open issues to address:

a. What to do with a new lot of panels to determine if these are similar to current panels?
b. How to assure panels are clean after each test cycle?

The next step included the peel adhesion test on a test panel with a known contact angle reference. A couple of common tapes were tested for peel adhesion on the panels.

With the information that the surface energy of the panels has increased with the lab ware cleaner, the peel adhesion testing resumed in an attempt to see differences among the cleaning methods. Three adhesive technologies were chosen; rubber, acrylic and silicone.

The panels were cleaned with the normal three solvent wash after the initial contamination wash. The tapes were applied to the panels with the normal 2 Kg roll down and after a 1 minute dwell, removed at 300 mm/minute. The results are shown in Table 4.

Table 4. Peel adhesion results with rubber and silicone based adhesives

180° Peel Adhesion					
Rubber Adhesive			Silicone Splicing Tape		
Units:	N/10 cm	Lb force/inch	Units:	N/10 cm	Lb force/inch
Alconox	8.89 ± .67	4.9 ± .37	Alconox	3.87 ± .07	2.13 ± .04
Contrex	8.53 ± .60	4.7 ± .33	Contrex	3.89 ± .03	2.14 ± .02
MEK	8.34 ± .40	4.6 ± .22	MEK	3.85 ± .05	2.12 ± .03

The rubber and silicone tapes showed high adhesion no matter the cleaning method. In the case of the rubber adhesive, a slightly lower value was found on the MEK washed panels, but values were within one standard deviation of the results. The measurements made with contact angle could provide a more precise indication of a clean surface.

An acrylic adhesive masking tape was tested with the following results (Table 5). With this tape, the MEK wash showed slightly lower values outside of the error of the standard deviation. A Student's t-test showed the MEK data was different from Alconox and Contrex. Another comparison of the Alconox and Contrex showed these results to be similar to each other.

Table 5. Peel adhesion with acrylic adhesive

180° Peel Adhesion		
Acrylic Masking Tape		
Units:	N/10 cm	Lb force/inch
Alconox	1.64 ± .098	.90 ± .054
Contrex	1.58 ± .071	.87 ± .039
MEK	1.39 ± .067	.77 ± .037

The increase in contact angle showed only slight differences in peel values at about 1.5 N/10mm. Even though a measurable difference could be found with contact angle, the effect on peel adhesion was minimal except with the lower adhesion acrylic tape. It is possible that with an even lower peel adhesion tape product the cleaning methods might produce an obvious difference in adhesion values. These panels have not been exposed to any other adhesives and the margin for error based on long term use needs to be studied for each lab based on the adhesives tested and cleaning solvent choices.

The objective of this study was originally intended to also look at older panel conditions, however, it was found during the course of initial panel cleaning that the number of variables in adhesive technologies and choice of solvents would make that study a huge undertaking in planning and resources to accomplish. The use of contact angle to determine the state of contamination can be used with old panels as well. Knowing that a lower contact angle represents a clean steel surface, a contact angle test before and after washing with a known solvent can provide information about how effective any particular solvent is at removing the PSA product completely.

Conclusion

There are several contributing factors to test panel reproducibility which we cannot control. The steel manufacturing plant controls the composition, annealing process, and final protective film for the stainless steel panels. The surface roughness is a result of the manufacturing process or an additional processing must be done to create a smoother finish before a testing lab utilizes the panel. The manufacturer's composition and resulting surface roughness are pre-determined. However, testing labs do have a significant amount of control over the conditioning and cleaning procedures of the test panel surface. The vast array of adhesive formulations combined with the buffet list of solvent choices to clean the panel provide the most opportunity for variation. In addition to a visual inspection, using contact angle to measure the surface energy, a known state of cleanliness can be measured.

For new test panels, cleaning with the Contrex or Alconox cleaner removes the residual manufacturing impurities and subsequently reduces the "break-in" period with new panels. Every lab controls solvent used and the diligence needed to produce a clean surface before each test. Using a high pH cleaner between different adhesive technologies can assist in removing residue from the previous test sample and provide an accurate measurement in the next test series.

This work is only a starting point. Additional work in these areas can be performed to better understand and validate best practices for removal of manufacturing contamination and complete adhesive removal for ongoing testing.

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References

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