

Corrosion Resistant Surface Finish by Chemical Browning

Final Report

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Abstract

The goal of this project was to create a uniform, corrosion resistant, brown finish for the Billy Bar grill cleaner using chemical methods. Three browning solutions and a browning procedure were found from literature. The samples were browned according to the procedure; two of the browning solutions produced a relatively uniform, dark brown finish, but the other resulted in a very splotchy finish. After browning was completed, the samples were placed into a humidity chamber to test the atmospheric corrosion resistance of the finish; unfinished control samples were also tested. EDS was used to characterize the finish produced by each browning solution. After the atmospheric test, two of the finished samples and the control samples were subjected to an immersion test in oxygenated water. All finished samples showed almost no evidence of rusting after the atmospheric test, and the unfinished samples only had small areas of rust. After the immersion test, however, the unfinished samples were rusted extensively; rust spots were present on one finished sample, but the other remained essentially free of rust. The finish on this sample (produced using solution 3) was the best overall, since it had a uniform dark brown color and showed excellent corrosion resistance. However, due to the complex and labor-intensive nature of the browning process, chemical browning is not strongly recommended as a method for producing a finish on the Billy Bar grill cleaner.

Table of Contents

Abstract.....	1
Introduction	3
Process	4
Sample Preparation	4
Chemical Browning Procedure	5
Atmospheric Corrosion Testing	6
Energy Dispersive Spectroscopy	7
Immersion Testing	7
Results.....	7
Discussion.....	13
Summary	15
Conclusions	15
References	16

Introduction

The Billy Bar is a revolutionary barbeque grill cleaning product made of AISI 1018 steel. The manufacturer has contacted us to develop an attractive, uniform, corrosion resistant coating. Two methods were put forth, one being a heat treatment in a fluidized bed to create a black coating, and the other a chemical means of applying a brownish coating. Our group was responsible for the chemically applied brown coating.

The first step was to pick several different chemical solutions based on their cost and complexity. Then the specific browning procedure was selected and the setup was decided upon. After the browning solutions were applied, the corrosion resistance of the coating was tested in an environmental chamber for two weeks under high humidity. The samples must not show any signs of significant corrosion in order to be considered for possible use. After the environmental testing, the samples were immersed in oxygenated water to simulate the sample's exposure to rainfall. Again, to be considered, the samples had to show no signs of corrosion to be considered. The manufacturer has also requested that we test whether abrasive surface preparation is necessary in order to achieve a good corrosion resistive layer. This was achieved by sandblasting some of the samples prior to chemical treatment. The coating of these samples was compared to the others to see if the step is a necessary expense.



Figure 1: Product image of the Billy Bar barbeque grill cleaner.¹

Process

Sample Preparation

Three different browning solutions were used to coat the Billy Bar sample. Multiple solutions were used in order to find the solution that created the most uniform coating, rust resistances and is the most visually appealing. The finished look and corrosion resistance behavior of the browning solutions listed in Table 1 are shown in the results section of this paper. These solutions were selected from an array of possible solutions found in the literature² based on two different criteria, namely their expected cost and chemical complexity. Due to time constraints, the number of solutions to be tested was reduced to three solutions.

The quality of the coatings was compared to each other and cost per gallon was taken into account along with complexity of the solutions. Simple solutions will be easier to make due to their lower complexity and will be cheaper since they contain fewer chemicals. At the same time the cost effectiveness of each solution is very important for saving money in the manufacturing process.

Each solution was applied to 3 Billy Bar samples. Two of the samples were 3 inches in length and the other was the full 16 inch length; the two sample sizes are shown in Figure 2. The smaller samples are being used in order to save raw material and space while still being able to see the effect of the browning solution. The smaller samples were prepared in two ways. One sample was sandblasted to remove any coating on the surface and create a clean, uniform surface for the browning to take place. The other 3 inch sample and the full length sample did not receive this treatment. The two small samples were boiled to remove grease and other contaminants while all of the samples were rubbed down with acetone and methanol. Once this surface preparation was complete, the browning process was undertaken.



Figure 2: Macrograph showing the two sample sizes which will be used for creating a brown surface finish.

Table 1: Composition of selected chemical browning solutions.

Component	Solution 1	Solution 2	Solution 3
Water	84.0	51.0	-
Ethanol	3.2	40.1	78.2
HNO ₃	8.5	-	4.3
HCl	-	-	7.5
Fe Cl ₂ 6	2.8	8.9	7.0
FeSO ₄	1.5	-	-
CuCl ₂	-	-	0.5
Iron filings	-	-	2.5
Cost Per Gallon (\$)	12	26	41

Chemical Browning Procedure

The first step (1) that was undertaken was the cleaning of the samples. One of the 3" samples was sandblasted and then boiled in clean water while the other 3" sample was just boiled. The full length sample was wiped down with acetone and methanol. This was done

because we did not have a beaker large enough to fully submerge the samples in. Once the samples were cooled, but were still warm, they were to be coated with the browning solutions (2). The 3" samples were dipped into the solutions for 1-3 seconds while the full length samples were coated using a cotton swab. This coat was then allowed to dry for around 30 minutes before a second coat was applied (3). After the second coat has dried for 30 minutes the samples were heated (4) to 140°F-145°F (dry heat) for close to 1 hr. Then after the sample has reached a uniform temperature the ammonium sulfate solution was placed into the oven to create a high humidity environment (5). The samples were kept in the oven for another hour and half before removing. The samples were then boiled again (6) in clean water for 15 minutes and then dried and carded (7) with a wire brush to remove any stray particles. The full length samples skipped step (6) entirely and were only carded before being coated with oil. Steps (2)-(7) were then repeated three more times for each sample before the samples were coated with oil (8).

The purpose of this browning procedure was to induce the formation of an oxide layer or rust on the surface of the sample. However, instead of a flaky oxide layer which is normally associated with rust, this procedure should result in an adherent layer that protects the underlying material from further oxidation.³

Some of the difficulties encountered with the browning processes were maintaining a high humidity environment at an elevated temperature. The hygrometer never recorded a humidity value greater than 50% at an elevated temperature, 140°F-145°F. At room temperature, humidity values close to 70% were obtained in the drying oven, but high humidity values were never obtained at higher temperatures. This could have been caused by temperature dependence of the hygrometer or due to a temperature dependence of the ammonium sulfate. The 3" samples dipped in solution 2 would also have their rust coating flake off whenever they were submerged in boiling water. This may have negatively affected the coating. The full length samples were too long for our current setup which created difficulties with both coating and cleaning and were therefore discounted for further testing. For a large scale production this problem could be easily fixed. The solutions were also weighed out taking the hydration into account though the literature weight percents most likely had accounted for this, leading our solutions to be stronger than called for.

Atmospheric Corrosion Testing

After the browning process was completed, the finished samples as well as two unfinished samples (to act as a control, one oiled, and one unoiled) were placed in a controlled-humidity atmospheric chamber. The purpose of the test was to evaluate the corrosion resistance of both the brown finishes produced by the three solutions as well as the bare metal finish of the control samples. The atmospheric chamber was constructed from a large Sterilite

box with a tight-fitting lid; a gasket was applied on the lip of the box to create an air-tight seal. The humidity in the chamber was maintained using a saturated solution of ammonium sulfate in a dish at the bottom of the chamber; 80% relative humidity was desired, but during the testing period, humidity levels were around 60-70%. For testing, the samples were suspended from the lid of the chamber using loops of fishing line which were fastened to plastic rods suspended across the chamber. A combination thermometer/hygrometer was placed inside the chamber to monitor the temperature and humidity during the test. The finished samples produced by all three browning solutions, the unfinished sample, and the heat-treated samples from the other MSE 489 group were tested concurrently. The corrosion test lasted for a period of two weeks and was conducted at room temperature. After the test was completed, the samples were removed from the chamber and examined to determine the extent and location of corrosion.

Energy Dispersive Spectroscopy

The boiled samples of solution 1, 2, and 3 had scrapings taken from their surfaces. These scrapings were then mounted with carbon tape onto an aluminum stage for the scanning electron microscope. In an effort to understand the chemistry of the coating, these samples were characterized by energy dispersive spectroscopy (EDS). EDS was performed at 20 and 25kV.

Immersion Testing

To simulate extended exposure to rain water, the sandblasted samples of solution 1 and 3, along with an oiled untreated sample and an unoiled untreated sample were suspended in a container filled with water which had an aerator connected to air in it. This setup exposed the samples to high amounts of oxygenated water. The samples were immersed for a period of 3 days. As with the environmental chamber, the extent of rusting was determined for each sample.

Results

The results from the browning process are shown in the following images. Figures 3-5 show the sand blasted, original, and boiled samples for each solution. The sand blasted samples are in the top of the images and the boiled on the bottom. An untreated sample is in the middle of the images to show the change that the browning procedure made on the surface of the samples.



Figure 3: Samples coated with solution 1 have a thick consistent layer.



Figure 4: Samples coated using solution 2 resulted in an inconsistent layer



Figure 5: Solution 3 samples have a thin but consistent layer

There did not appear to be a difference between samples that had been sandblasted and those that had been boiled. Solution 2 provided a blotchy layer on the sample and

therefore is not an option for the tool. Solution 1 and 3 both created consistent finishes that met the requirements. The following images are close-up shots taken for each of the sand blasted samples. These show in better detail the coating placed on the surface.



Figure 6: Solution 1, good layer consistency



Figure 7: Solution 2, very blotchy thin layer, not a good choice



Figure 8: Solution 3, thin but consistent layer

Following browning, the samples were placed into a humidity chamber for atmospheric corrosion testing. The images in Figures 9-12 show the results of this test. The following abbreviations were used for labeling the samples: S# indicates which solution was used followed by a suffix to indicate surface preparation (S-sandblasted, B-boiled). For the untreated samples the prefix U was used while the suffix referred to finishing (U-unoiled, O-oiled).



Figure 9: Solution 1 samples showing no rust formation except the lower ring.



Figure 10: Solution 2 samples showed no rust except on the bottom of S2-B



Figure 11: Solution 3 samples have no rust except the ring near the bottom.

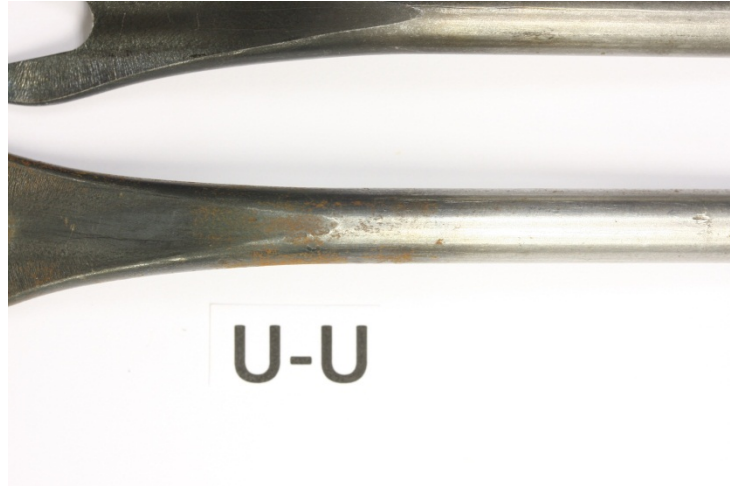


Figure 12: U-U sample which shows a small amount of rust formation near the neck of the sample.

Following the atmospheric corrosion testing, sandblasted samples from solution 1 and 3 along with an oiled and unoiled untreated sample were immersed in oxygenated water. The results from this test can be seen in Figures 13-15.



Figure 13: S1-S sample shows many rust spots. S3-S sample has no rust formation on the head and shaft except the unexplained ring located near the bottom



Figure 14: U-O sample shows some rust prevention from the tung oil.



Figure 15: U-U sample has significant rust formation.

Discussion

Our goal was to provide a corrosion resistant layer that is resistant to wear and uniform in color. The corrosion resistance of the samples was tested using a high humidity atmospheric chamber. Based on the requirement for a uniform surface finish it was determined that solution 2 was not acceptable. It resulted in a thin very blotchy surface coating that was unacceptable for the Billy Bar. During the dry heat curing procedure; it became brittle and flaked off during boiling. Solution 1 and 3 provide promising results in regards to uniformity. Solution 3 did however provide only a thin layer to the surface due to the high concentration of

HCl in the solution. The solution did well after the first cycle of the procedure. It wasn't until the second cycle that we realized the solution was so strong that it strips the previous layer off during re-dipping for a second coat. Due to this constant "re-stripping" the coat may be thin and ultimately means that any further processing is wasted time and resources. Solution 1 provided a thick black uniform layer which took several coats to achieve.

All of the samples were placed into an atmospheric testing chamber with ~65% humidity for two weeks following coating. All of the solutions showed little to no corrosion. Several of the samples showed a thin ring of rust around the bottom of the shaft which can easily be seen in the S3-S sample of Figure 11. These rings were not exclusive to one solution and were not specific to one pretreatment. They were not found on both of the uncoated samples. The tung oil did not seem to affect whether or not this ring formed. We do not know what caused this ring to form or why its choice of sample substrate was unspecific. The U-U sample showed a small amount of rust formation near the neck in Figure 12.

The samples of solution 1 and 3 along with the uncoated samples were placed into the immersion chamber. Solution 1 and 3 sandblasted samples showed little to no rust as seen in Figure 13. Solution 1 was the worst of the two which formed small specks of rust randomly around the sample. Solution 3 had no rust formation and consequently is the number one choice because of its corrosion resistant uniform layer. The two uncoated samples showed significant amounts of rust formation which can be seen in Figure 14 and 15. The uncoated-unoiled sample had the greatest amount of rust which was to be expected. The tung oil alone prevented a large portion of the rust from forming.

EDS results were inconclusive. Sulfur was observed in the scrapings taken from the sample that had been treated with solution 1, which contained sulfur. All the scrapings, with the exception of some taken from solution 2 showed the presence of oxygen. The lack of oxygen on some of the filings for solution 2 could have been due to its splotchy, uneven nature. Iron was present in all of the samples as would be expected from steel. It was impossible to tell if it was the coating that was being analyzed based on the scrapings that were created. A better way of going about characterizing the coating would have been to section the sample and analyze the coating in cross section.

Cost analysis shows that Solution 3, the best in terms of both uniformity and corrosion resistance, costs around \$41/gallon, while solution 1, the second best option, costs close to \$12/gallon. While the solutions seem expensive, very little is actually used for each coating and the solutions can be reused extensively. The cost could also be considerably lower if the chemicals are purchased in bulk.

Summary

Three browning solutions were selected from those found in literature, based on their projected cost and complexity. For each browning solution, three samples were prepared: a full length sample (the whole Billy Bar) and two short samples cut from the tip of the Billy Bar. Of the two short samples, one was sandblasted before proceeding with browning to determine whether this step affected the quality of the finish. The samples were then browned according to a procedure found in the literature. Several difficulties were encountered during browning, mainly maintaining high humidity in the rusting chamber. After browning, the short samples from Solutions 1 and 3 exhibited a uniform, dark brown coating, but the short samples from Solution 2 had an unattractive, splotchy finish. Due to a lack of proper equipment, browning could not be completed satisfactorily for the full-length samples. The coated samples were then subjected to a two-week atmospheric corrosion test in a humidity chamber; uncoated control samples were also tested for comparison. After the test, all of the coated samples showed almost no evidence of rusting, and even the uncoiled control sample had only light rust. For this reason, it was suspected that the tung oil applied as the last step of browning was mostly responsible for the observed corrosion resistance. EDS was performed on samples of the coating produced by each browning solution to determine whether the chemistry of the solution affected the coating. However, the method used to obtain the EDS samples (scraping) did not yield very good samples of the coating, so the EDS results did not provide as much information as expected. As a further testing step after the atmospheric corrosion test, the sandblasted samples from Solutions 1 and 3, along with the control samples, were subjected to a three-day immersion test in oxygenated water to simulate exposure to rain. The results of this test were more definitive: both control samples had extensive areas of rust and the Solution 1 sample had small spots of rust in several areas, but the Solution 3 sample showed essentially no evidence of rusting.

Conclusions

The conclusions we have reached are enumerated below. These conclusions were reached following the processes and characterization method mentioned earlier.

- (1) Solution 3 provides the most corrosion resistance and uniform coating
- (2) Coating chemistry/composition needs to be further characterized
- (3) Implementing this process would require the purchase of a good amount of equipment
- (4) Process is labor intensive, inconsistent, and complex
- (5) Sand blasting the samples did not have a noticeable effect on corrosion resistance

Due to these factors, we do not recommend this process to create a corrosion resistant coating for the Billy Bar. There may be other, better ways of accomplishing this task that should be explored.

References

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