A WATER BASED MASKANT BECOMES MORE USER FRIENDLY

Thomas D. Brown
Principal Engineer/ Scientist
Boeing Phantom Works, Long Beach Division
Long Beach, California

Jo Ann Garner
Engineer Scientist – Specialist
Boeing Information, Space, and Defense Systems Division
Huntington Beach, California

ABSTRACT

The Chemical milling process for aerospace parts began in the early 1950’s using solvent based maskants. Some eight years were spent on improving these maskants until the only major problem facing them was the air contamination from the solvents. With the hope of equal performance the maskant manufacturers began developing water based maskants. However, uniformity was difficult to maintain with the water-soluble resins. This paper will describe one of the latest candidates for a user friendly water based maskant at Boeing Long Beach Division.
INTRODUCTION

Artisans have etched metals since the Middle Ages when they used acids to etch patterns on the knights’ armor. In the more recent past, 1954 to be exact, a company involved in developing the chemical milling process used an existing aluminum etchant that served as the prototype for the later developed chem mill etchants. Once effective etchants were produced, it was found that the key to successful chemical milling was the maskant.

The maskant has to adhere to the unetched area of the part in the etchant but be easily scribed and stripped on those areas that are to be etched. Then when the etching is completed, it has to release from the surface so that it can be easily and completely stripped, by hand.

Solvent based protective coatings were the norm in the 1950s in all industries that used them. The chem mill industry did not depart from this common, accepted norm. At the time, there was initially a neoprene based solvent maskant for aluminum and a butyl based solvent maskant for steel and titanium. Most of these solvents were environmentally destructive. Using vapor degreasers for parts cleaning also contaminated the atmosphere.

California’s environmental laws regulate and restrict the release of certain manufacturing chemicals into the environment via the air, water, or soil. In response to these laws, The Boeing Company, Long Beach Division (Boeing, LBD) has replaced its solvent based chemical milling maskant with a water-based maskant.

Many companies use water based maskants on small parts. LBD is using a water based maskant on large airplane skins which can measure 12’ x 40’. One of the major problems Boeing-LBD is facing in its maskant/chemical milling process is the variation of the adhesion properties of the maskant to the aluminum substrate. At times the adhesion is too strong and the operators cannot easily remove the maskant; at other times the adhesion is too weak and the maskant sloughs off the aluminum substrate during the chemical milling process.

Prior laboratory testing at both the vendor and Boeing, LBD indicates that the surface finish of the part after cleaning is a contributing factor to this adhesion problem. Cleaning procedures and materials had also changed from the inception of chemical milling. California environmental regulations have forced changes to the cleaning procedures and chemicals used to clean parts. The cleaned metal surface of today is quite different from the cleaned metal surface of the 1950s. Laboratories can simulate the cleaning processes but they cannot duplicate the balance of chemicals and contaminants found over time in the large 80,000 gallon tanks used in the Production Cleaning Line at Boeing LBD. This joint work proposal between the vendor and Boeing LBD evaluates the newly formulated water based maskant. It addresses the surface finish of the aluminum after cleaning in production tanks and its affect on the adhesion properties of the water based maskant. Optimal maskant cure temperatures is also addressed. This new maskant requires no topcoat. The elimination of the topcoat application step as well as the procurement of the topcoat material will be a time and cost savings advantage to Production.

At Boeing, LBD the chemical milling maskant is required to perform many different functions. It must act as a protective coating on parts as they are
being transported from station to station often between buildings in all types of weather. During stretch forming, the maskant must act as a lubricant between the template and the metal. It must also be elastic enough to survive the stretch form process, yet remain attached to the metal skin. The maskant must adhere strong enough to survive the chemical milling process, yet be easily removed as each step is exposed to the etchant solution. The maskant must be able to operate in both the Type I (4L) etchant solution and the Type II (17L) etchant solution. Finally, the maskant must survive the anodize process, protecting those areas not to be anodized before complete removal is attempted. On top of all these requirements, the maskant itself must be environmentally compliant. Waterbased maskants have had a difficult time complying with each of these functions. We think we've found one that does well in each of these categories and very well in several of them.

TEST PROGRAM

The primary thrust of the program was to determine the effectiveness of the new maskant under various cleaning processes and material alloy conditions. The maskant was designed for alkaline cleaned surfaces with unique adhesion characteristics. The process of chemical milling usually requires multiple sequential removal stages. At each stage, maskant must be removed from the surface where the next cut is to occur. If the adhesion is too low, the pulling of the sequential cuts is very susceptible to ‘pull ups’ or lifts on the remaining maskant lines. The chemical milling outgassing process can catch the edges of the maskant and blow off the deep cut lines. A chem mill maskant should adhere to the surface and not be easily pulled up while removing the sequential step cuts. On the other hand, when the chem mill process is complete and the maskant needs to be completely or partially removed, the maskant should quickly release and easily tear into removal strips. This maskant was designed with these criteria in mind. It is referred to as the “adhesive – snap” characteristic. The slow peel, or low shear strength adhesion, is desired in the one to three pounds per inch adhesion range (16 – 48 ounce / inch) while chem milling is taking place. The adhesion should drop very low and “snap” off (fast peel or high shear strength adhesion) as the sequential steps are being removed and at the end of the process when large quantities of maskant need to be removed. This maskant was modified to have just such a shear relaxation effect.

The evaluation was separated into 2 sections. The first section was comprised of 4 groups of 0.125” x 12” x 12” specimens.

Group 1, 2024-T0, bare aluminum
Group 2, 2024-T3, alclad aluminum
Group 3, 7075-T6, bare aluminum
Group 4, 2024-T0, bare aluminum which had been heat treated and stretch-formed in-house, ending up in the T42 hardness form.

The second section consisted of production sized skins (0.0” x 69” x 235” and 70” x 113” x 300”) of 2024-T3 alclad aluminum.

The test matrix is outlined in detail in the following section and summarized in Table #1. (NOTE: Unless otherwise noted, all specimens were processed through the large production tanks.)
**TABLE #1**

Test Matrix

<table>
<thead>
<tr>
<th>ID</th>
<th>Aqueous Degrease 160 F</th>
<th>Alkaline Clean 135 F</th>
<th>Acid Etch Ambient</th>
<th>Deox. Ambient</th>
<th>Conversion Coating ≤ 140 F</th>
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<tr>
<td>A</td>
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<tr>
<td>K</td>
<td>X</td>
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</tr>
</tbody>
</table>

**PROCESS PROCEDURES**

**PROCESS ‘A’:**
- a) Aqueous degrease specimens 30 minutes followed by a hot DI water rinse and spray.
- b) Alkaline clean specimens 10 minutes followed by 2 rinses.
- c) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.

**PROCESS ‘B’:**
- I a) Aqueous degrease specimens 30 minutes followed by a hot DI water rinse and spray.
- b) Alkaline clean specimens 10 minutes followed by 2 rinses.
- c) Acid etch for 10 minutes followed by a spray and immersion DI water rinse.
- d) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.

**PROCESS ‘C’:**
- a) Aqueous degrease specimens 30 minutes followed by a hot DI water rinse and spray.
- b) Alkaline clean specimens 10 minutes followed by 2 rinses.
- c) Immerse in the Deoxidizer for 10 minutes followed by a spray and immersion DI water rinse.
- d) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.

**PROCESS ‘E’:**
- a) Aqueous degrease specimens 30 minutes followed by a hot DI water rinse and spray.
- b) Immerse in the Deoxidizer for 10 minutes followed by a spray and immersion DI water rinse.
- c) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.

**PROCESS ‘F’:**
- I a) Aqueous degrease specimens 30 minutes followed by a hot DI water rinse and spray.
- b) Alkaline clean specimens 10 minutes followed by 2 rinses.
- c) Acid etch for 10 minutes followed by a spray and immersion DI water rinse.
- d) Conversion Coat per Mil-C-12345, Class 1A
- d) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.

**PROCESS ‘G’:**
- a) Aqueous degrease specimens 30 minutes followed by a hot DI water rinse and spray.
- b) Alkaline clean specimens 10 minutes followed by 2 rinses.
- c) Immerse in the Deoxidizer for 10 minutes followed by a spray and immersion DI water rinse.
- d) Conversion Coat per Mil-C-12345, Class 1A
- e) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.

**PROCESS ‘J’:**
- a) Aqueous degrease specimens 30 minutes followed by a hot DI water rinse and spray.
- b) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.

**PROCESS ‘K’:**
- a) Alkaline clean specimens 10 minutes followed by 2 rinses
- b) Air dry specimens, wrap in neutral Kraft paper, and return to Lab to hold for masking.
MASKING OF 12" x 12" SPECIMENS:
Processed specimens were transported down to the Vendor facility for masking. The maskant tanks and oven were larger and groups of 12-48 could be processed simultaneously. Each specimen was processed through 2 maskant cycles.

One cycle consists of the following:
1) Dip specimen, by hand, into the maskant at a rate of approximately 12" per minute.
2) Allow to air dry for a minimum of 15 minutes and no longer than 30 minutes.
3) Transport to a drying oven set at 185 ºF and cure.
4) Allow specimens to come to room temperature before re-dipping or testing.
The cure time at the end of the first cycle was 3 hours. The cure time at the end of the second cycle was 2 hours.

Two adhesion pull tests were conducted and reported, one after the second cure after the specimens had returned to room temperature and one 3 days later. Each alloy tested had 3 specimens per process. The reported adhesion values are the averages of these 3 specimens.

PROCESSING OF LARGE SKINS:
Process large skins on Boeing-LBD’s Production Lines using Process ‘A’.
Using appropriate protective coverings and transport racks, transport to Vendor’s facilities for maskant application.

Spray apply two coats of the maskant to all sides, curing at 185 ºF for 3 hours after the first coat and 2 hours after the second coat. Protectively wrap and transport back to Boeing-LBD.

Stretch form the skins on the appropriate stretch form dies. Laser scribe the given pattern on the concave side of the skin, sealing the scribe lines with 2 coats of the silicone sealant. (NOTE: some skins sat around for as many as 90 days before the stretch formed skin was laser scribed and chem milled.)

CHEMICAL MILLING OF MASKED SPECIMENS
Sections of maskant were removed from each specimen, exposing the aluminum substrate. Specimens were racked vertically with enough space between each specimen to allow free solution movement around each part while immersed in the selected chemical milling solution.

The 12" x 12" test panels were immersed for 45 - 60 minutes in either the 4L/Type I etch solution or the 17L/Type II etch solution.

The large production skins were laser-cut and step etched; immersion times varied depending on the depth of cut called out in the production order. Up to 10 multiple cut cycles were performed on each skin. After chemical milling, specimens were rinsed, desmutted for 10 minutes in the Desmut (Deoxidizer) solution, rinsed again and allowed to air dry. When the final cut cycle had been completed, the maskant was removed and the line quality was observed.

DISCUSSION
Panel set ‘A’ represents the most common cleaning preparation sequence utilized in the aerospace industry. This is an immersion in aqueous degreaser solution, warm water rinse followed by an alkaline immersion cleaning cycle. This represented the base line production cleaning process by which to measure maskant performance (adhesion, peel release and chem mill quality).

Panel sets ‘B’ continued the alkaline cleaning process into a 1051 acid etch solution. This type of cleaning has been used to help remove scale from heat-treat
or activate the metal surface for subsequent Conversion Coat coatings. It is known to create higher adhesion surfaces on bare aluminum and very low adhesion surfaces on clad aluminum surfaces.

Panel set ‘C’ used the alkaline based, line cleaning process but then followed with a Deoxidizer immersion to remove any alkaline residue left from the process and de-activate the metal surface. Deoxidizer immersion is sometimes used as a quick cleaning technique in chemical milling to remove surface contamination just prior to masking.

Panel set ‘E’ was used to investigate the effect of bypassing the alkaline cleaning tank using just the aqueous degreaser followed by the Deoxidizer technique.

Panel set ‘F’ represents the technique utilized in the past with solvent maskants to improve adhesion and line quality on clad or deep cut aluminum substrates. This is included for completeness of the possible variations available. The application of chromated conversion coatings is being phased out of most facilities due to environmental concerns.

Panel set ‘G’ used an aqueous degreaser found on the hand processing line for comparison to panel set ‘F’ and utilized the Deoxidizer solution instead of the acid etch. The acid etch solution is known to increase adhesion. It was decided to test the effect of using the Deoxidizer solution in its place for relative performance effects.

Panel set ‘J’ was used as a base line to determine the effects on adhesion with only aqueous degreaser cleaning. This would simulate a panel being miscued and masked before it finished the cleaning process. It was also used to determine the effect of residual degreaser by-products that may be left on the metal surface after processing.

Panel set ‘K’ was to complete the base line of ‘J’ by having the aluminum alloys cleaned only through the alkaline cleaning solution.

It is important to note that these test panels and the subsequent large stretch formed production parts were processed on the Boeing production line in Building 6 for stretching, heat-treat, and aqueous degreasing, then transported to Building 5 for the remaining cleaning – milling processes. The panels contained streaks and residue from the cleaning process (and even a tennis shoe footprint) due to rinse and handling anomalies, issues that will be addressed by the Boeing-LBD facility separate from this project. These were not pristine special care panels. One set was even lost for 4 weeks and is included in the data set for comparison to its replacement set which was processed in a normal time sequence.

The large production parts, which were stretch formed and chem milled, exhibited the same adhesive - snap characteristics as the 12” x 12” test coupons. The shop personnel were very complimentary on the dual adhesion characteristics of the new maskant - higher slow peel for step cut removal and the very easy snap quick release peel when stripping the skin. The production parts were milled in the 4L/Type I etchant with 10 step cuts. Silicone was used as a line sealer for the multiple laser cuts. No maskant leakage or penetration was found on the parts (test panels or large production parts). The maskant performed with excellent results.

RESULTS

Adhesion results are graphed in the charts. All processes worked very well on
all metal alloys tested and none of them had high or difficult adhesion.
The best overall cleaning process was the normal aqueous degreaser followed by the alkaline cleaning process (Panel Set ‘A’).

The acid etch process (Panel Set ‘B’) had the highest initial adhesion on T0-bare and heat-treated metal and low adhesion on clad surfaces after relaxation.

The Conversion Coated surfaces (Panel Sets ‘F’ & ‘G’) had slightly higher adhesion values than their non-conversion coated counterparts (Panel Sets ‘B’ & ‘C’). All were within acceptable adhesion ranges.

Set ‘C’, where the Deoxidizer appears to be doing a clean up job was lower in relative adhesion. This lower relative adhesion was also noted in Set ‘G’ where the Conversion Coating was used in conjunction with the Deoxidizer. Where the Conversion Coating was used in conjunction with the acid etch, the adhesion was higher.

The stretch forming operation of the large skins was performed without using oils or talc on the stretch form die. Kraft paper was used at the edge of die to minimize edge damage to the maskant and to lower friction.

All panels tested after the chemical milling process were in the acceptable adhesion range and demonstrated the easily stripped, snap-release property of the maskant.

The line edges after chem milling were sharp and satisfactory in both the 4L-Type I and 17L-Type II etchant solutions.
CONCLUSION

The adhesion characteristics under the various production cleaning process were excellent and within acceptable manufacturing ranges. Aqueous degrease followed by alkaline cleaning appears to be the most effective process across all the alloys and heat-treated materials evaluated. A conversion coating or acid etch preparation were not needed to yield proper adhesion performance during chemical milling.

Large (0.170" x 113" x 300") production parts coated with this maskant went through stretch forming operations without the use of oils or talc's on the stretch form die or mid-skin tearing of the maskant during the stretch operations. Masked test parts were successfully processed through both the 4L/Type I and 17L/Type II chemical etch solutions without difficulties. The maskant was compatible with the silicone based line sealant material used during the chemical milling process. The maskant was easily removed after the chemical milling had been completed and yielded good quality multiple cut chemical milling lines. All testing was successfully conducted without the use of a topcoat or seal coating.

The new waterbased maskant appears to be a major improvement over its predecessors and successfully works under production conditions. The elimination of the topcoat application step, as well as the procurement of the topcoat material, is a time and cost savings advantage to Production.

PRODUCTION SOLUTIONS

The initial charge for all tanks is done with DI water, which is kept at ≤10 PPM. The water used on all production spray and overflow rinses comes in at ≤100 PPM.

AQUEOUS DEGREASER
Daraclean 238: W. R. Grace & Co.
Conc.: 15 – 18 % v/v

EZE 206K: Calgon, Inc
Conc.: 15 – 18% v/v

ALKALINE CLEAN
Ardrox 6471: Brent America Inc.
Conc.: 10 – 24 fl. oz./gal.

ACID ETCH
19c etch: The Boeing Company
Chromic Acid
Nitric Acid
Hydrofluoric Acid

DEOXIDIZER (Desmut)
Turco Smut-Go NC: Elf Atochem North America Incorporated
Conc.: 7.5 – 10.5 oz/gal.

Conversion Coating
Alodine 1500: Henkel Surface Tech.
Conc.:1.1 – 1.5 fl. oz/gal.

WATERBASED CHEMICAL MILLING MASKANT
CAX-200-NS: Malek LLC, Inc.
Conc.: 100%

TYPE I, CHEMICAL MILLING ETCH
4L/Type I Etch: D.C. Atkins and Son
Conc.: 40% v/v

TYPE II, CHEMICAL MILLING ETCH
17L/Type II Etch: The Boeing Company
Sodium Hydroxide
TFE #3
Triethanolamine
Photo 1
Loading large production parts masked with CAX-200-NS on stretch press

Photo 2
Complex contour stretch formed masked part 113” X 300” X 0.170”
Photo 5
Backside and End view of Complex contour stretched masked production part
Photo 6
Stretch Formed and Type I (4L) chem milled production part 69” X 235” X 0.160 masked with CAX-200-NS

Photo 7
Complex cut on Clad Surface Type II (17L) Etchant  

Photo 8

2024-T42 heat treat alloy Type II (17) Etchant  

Photo 9