"A Non-Chromium, Non-Heavy Metal Deoxidizer System for Aluminum and its Alloys "

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ABSTRACT

This paper will describe a two-step, non-chrome, non-heavy metal deoxidizer system now commercially available which, when used prior to chrome conversion coating of 2024 T-3 and other aerospace alloys, meets all the requirements of military and commercial aerospace specifications. The first step of the deoxidizer system has cleaning capabilities, and when it is used following a suitable aqueous degreaser, the traditional phosphated-silicated alkaline cleaner is not necessary.

Data will be presented on bare and painted corrosion resistance tests as well as paint adhesion tests. This deoxidizer system can also be used prior to anodizing, welding/brazing, or other processes which must meet military or commercial aerospace specifications.

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Background

In spite of the importance of deoxidizing and desmutting in aluminum finishing, literature on the subject is somewhat sparse. Even some of the best books on aluminum finishing devote little space to deoxidizing or desmutting. For example, the 1987 edition of Wernick, Pinner, and Sheasby[1] (a two volume set, 1325 total pages) devotes 1 1/2 pages to desmutting, which is an improvement over the earlier editions of Wernick and Pinner[2]. Brace and Sheasby[3] devote 5 pages. Very few papers have been published which are strictly devoted to deoxidizing, although some, such as Ketcham and Brown[4], and Mohler[5], included deoxidizing variables in their studies, and in 1975 Smith[6] wrote an excellent article on deoxidizing.

Deoxidizing has not drawn the attention that some of us would like to have seen because deoxidizing/desmutting of the majority of wrought aluminum alloys is not difficult. Many shops use commodity baths based on nitric acid, nitric + sulfuric acids, nitric acid with fluoride, or proprietary baths based on ferric sulfate with nitric or sulfuric acid, or sulfuric acid/hydrogen peroxide mixtures. These solutions are quite adequate for most aluminum alloys. However, the aerospace industry has a unique problem in having to process highly alloyed materials.

In order to achieve the necessary mechanical properties to allow aluminum to be used in critical aerospace applications, aluminum must be alloyed with other elements. Unfortunately for the manufacturers and users of aerospace equipment (and fortunately for chemical suppliers and waste treatment equipment suppliers), the majority of aerospace aluminum parts are necessarily made with alloys containing copper.

As most aluminum finishers in the aerospace industry know, the wrought aluminum alloys which present the biggest deoxidizing/desmutting problems are those which contain copper. The reasons for this fact are related to the two metals' position in the electromotive series. Aluminum and copper are quite far apart, and aluminum is on the anodic side, while copper is cathodic; this means basically that there is a strong tendency for galvanic corrosion to occur, and aluminum will have a tendency to dissolve. Metallurgically, copper and aluminum do not mix together very well, and aluminum/copper alloys tend to have copper and copper intermetallics dispersed as aggregates within the aluminum. Areas of high copper concentration become excellent sites for galvanic and pitting corrosion to occur.

The information we have presented thus far is a review of facts known since aluminum/copper alloys were developed during World War II. Aluminum finishers of the post World War II era soon found that addition of Chromic acid or other chromates to their deoxidizer tanks prevented pitting corrosion and enabled them to meet military and aerospace specifications for corrosion resistance of finished aluminum parts, when used in conjunction with good quality chromate conversion coatings or anodize.

Through the 1950s and -60s improvements were made in chromated deoxidizers, and the technology peaked following a patent by Dollman[7] in 1970 involving the addition of a ferricyanide salt to precipitate dissolved copper and other alloying elements which affected the successful operation of the bath at levels as low as 200 ppm. This invention resulted in an increase in deoxidizer bath lives of three to four times over previously available technology. Not only did this result in saving of recharging costs, but through the 1970s and beyond when chromium-containing sludges were identified as hazardous waste, waste treatment cost savings were also realized. Unfortunately we now know that ferricyanide has joined chromium as being extremely hazardous and is quite difficult to treat prior to disposal.

Until now no one has been able to successfully replace chromated deoxidizer technology for critical applications. The only available non-chromate deoxidizers which came close to their performance were those based on ferric sulfate, which were patented in the 1960s [6, 8]. However, for critical applications such as chromate conversion coating, iron-containing baths are inconsistent and potentially risky, considering that free iron is a contaminant in a chromating bath (our company recommends 10 ppm maximum free iron), and even minor dragout problems can result in loss of that bath in a short time.

One unique chrome-free deoxidizer which is worthy of mention was developed by Batiuk[9]. His idea was to follow a non-chrome, iron based deoxidizing solution with a solution which would complete the deoxidizing; that is, oxidize any residual alloying elements on the surface to their more soluble state. Batiuk's system had some disadvantages, however. First, his system used salts of nitrites, which can contribute to the formation of carcinogens. Second, the data which he presented in his patent, in which he followed his deoxidizer with chromate conversion coating, indicated that he was able to pass the salt spray requirements of Mil-C-5541, (168 hours), but not the requirements of Mil-C-81706, (336 hours). However, Batiuk's concept of deoxidizing in two steps was recognized as highly feasible and shown to be practical by McMillen[10,11], whose work was the basis for the presently described system.

The system described by McMillen was quite successful in the laboratory, but when it was tried in field tests in cooperation with the Boeing Co., a number of changes were found to be necessary by Carlson[12,13], due to failing intergranular attack and end grain pitting tests. Carlson's optimization of the process produced results which showed that the performance of a chromated deoxidizer could be matched by a two-step, non-chromated system.

<u>Deoxidizing vs. Desmutting</u>

Before we present a description of our new system, it will be helpful to distinguish the difference between deoxidizing and desmutting. The following definitions describe the difference between the two:

> **Deoxidizing** is defined as: **the removal of oxides and other inorganics which would interfere with normal finishing procedures.**
>
> **Desmutting** is defined as: **the removal of pretreatment residues without significant attack on the surface of aluminum.**

For relatively pure alloys where oxides of aluminum or magnesium are the materials which must be removed, mineral acids such as nitric or sulfuric will dissolve them. When the surface inorganics are not very soluble in mineral acids, as with 2xxx series alloys, the addition of fluoride and an oxidizer such as hexavalent chromium must also be present. There is a perceptible but controllable attack on the aluminum surface by deoxidizers, and some include this parameter, usually termed "etch rate", in their processing control procedures. We use the term "etch" with caution, since we do not want to confuse the term with the etch of alkaline etchants, where the etch rate, or chemical attack, is at least ten times that of a deoxidizer. Deoxidizing is necessary almost anywhere, any time that surface impurities might interfere with further processing.

Actually, desmutting is a special type of deoxidizing, as pretreatment residues (smut) are "other inorganics" on the surface. However, most solutions termed "desmutters" normally have a much lower etch rate than those solutions we call "deoxidizers". Desmutters normally follow an etchant (alkaline <u>or</u> acid) and remove those reaction products or alloying constituents which are insoluble in the etchant.

Deoxidizing is an integral part of a number of operations involving aluminum for Aerospace. A list of typical operations where deoxidizing is needed is shown in *Figures 3 and 4*[14]. The most critical operation in terms of imparting satisfactory corrosion resistance and paint adhesion properties is conversion coating, and most of our discussions from here on will involve conversion coating.

The Deoxidizing System

Now let us look at our new deoxidizing system. Note that I have used the word "system". The reason for this, which we must emphasize, is that the deoxidizing is done in two steps: an acid etch/cleaner, which removes aluminum and magnesium oxides but leaves a smut of most of the other alloying elements, and a desmut solution, which completes the oxidation of the other alloying elements to their more soluble ionic states.

It might be helpful at this point to look at what a deoxidizer does to an aluminum alloy surface. *Table 1* represents the results of a surface analysis performed by Auger Electron Spectroscopy by Dr. Jack Kramer of our Analytical Department[15]. Sample 1 represents a "Cleaned Only" surface; a bare 2024-T3 panel was immersed in a silicated\phosphated cleaner, rinsed with deionized water, and air-dried. The magnesium, aluminum, and oxygen, represented here were actually oxides of these metallic elements. The oxide layer was quantified by depth profile as being about 900 Å thick, and masks any copper which might be present on the metal surface. The other elements represent residuals from the cleaner. Sample 2 data represents another bare 2024-T3 panel, cleaned, then deoxidized in our non-chrome system, rinsed in deionized water, and air dried, and Sample 3 was similarly processed except that the deoxidizer in this case was our best chromated product.

Note the similarity between the results of the two deoxidizers. The magnesium is entirely gone. There is still aluminum oxide on the surface, but the thickness is only 60 Å. It may be surprising to some that we now have some copper on the surface. The depth profile shows that the copper layer is about 120 Å. It is important to note that analyses over several points on the panel indicate that the copper is present over the surface of the panel in the same 120 Å thick layer. Removing <u>all</u> of the copper is not possible, but it is only when the copper on the surface is present in clusters or agglomerates that potential galvanic and pitting corrosion sites are available.

Now let us look at the deoxidizer solutions in more detail:

1. **Acid etch/clean-** a fluoride-containing acid solution which attacks the aluminum surface at a highly controllable rate. The optimum etch rate has been found to be equivalent to the etch rate of chromated deoxidizers. As the name implies, this solution has a built-in acid stable surfactant which gives the solution cleaning capability. Other than aluminum, which dissolves in the solution at a slow rate, and trace quantities of alloying elements, there are no heavy elements in this bath. It is important to note, as seen in *Table 2*, that copper is hardly soluble at all in this solution. The data in *Table 2* was generated by processing only bare 2024-T3 panels through this solution[16].

2. **Desmut** - As we have said, the alloying elements and intermetallics in 2024-T3 and other aerospace alloys are not very soluble in the acid etch/cleaner. Copper is oxidized to the +1 state and exists as Cu_2O on the surface, and some iron oxidizes to Fe^{+2} and exists as FeO. The insoluble smut products are removed in a desmutting solution, based on nitric acid with an oxidizer, which converts the insoluble reaction products to their more soluble oxidation states, such Cu^{+2} and Fe^{+3}, thereby removing them from the surface. As also seen in *Table 2*, the buildup of dissolved aluminum or copper in this bath is quite small. Remember that this was a panel study where dragout was minimal, and if actual parts with higher dragout rates were run, buildup would undoubtedly be much slower.

Control of both of these baths is quite simple, involving testing which is no more difficult than control of chromated deoxidizers. We should mention that the fluoride content of the acid cleaner bath is quite low, and can be adjusted to modify the etch rate, as necessary.

The desmut solution is controlled with a simple acid titration and an iodometric oxidizer titration. Temperature control is not necessary on this bath. Both tanks are mainly replenished with two packages (a third package, an optional surfactant package, is available to improve cleaning capability of the acid etch/cleaner). Details are shown in *Figure 5*.

Bath life of both solutions has proven to be extraordinary. One would particularly wonder about the life of the acid etch/cleaner since we have already acknowledged that there is a slow but definite dissolution of aluminum in this bath. In the bath described in *Table 2* a sludge began to form at an aluminum level of 1200 ppm, but no panel failures were experienced when panels were further processed and tested. The sludge was identified as aluminum fluoride. Since the bath will operate successfully even when saturated with aluminum fluoride, the sludge can be continuously filtered or removed on a periodic basis.

Figure 6 shows the bare panel tests which all pass using this deoxidizer system. With a good quality conversion coating on 2024-T3 panels we have not only been able to consistently achieve passing 336 hours neutral salt spray, but passing results of over 1500 hours exposure (of <u>bare</u> panels) are common. Since most aircraft are painted, it is also important to consider properties of painted surfaces. A list of paint adhesion and corrosion resistance tests run is shown in *Figure 7* and shows passing results in all cases. These results were obtained with a typical aerospace paint system consisting of an epoxy primer and an epoxy polyamine topcoat specified in Boeing Specification BMS 10-11[17].

When operating a chromated deoxidizer, it is very important to know the copper content of that bath to successfully process parts through that bath. With this in mind, we tried to get an understanding how this system would operate with dissolved copper in the baths even though we could not get copper to dissolve in the acid etch/cleaner bath by running 2024 parts. The acid cleaner bath was doped with copper sulfate such that the copper level was 450 ppm. While processing panels through this bath the smut was a distinct metallic copper color. The copper level of the desmut bath rose to 260 ppm before it could no longer remove this copper smut. However, panels processed through this system and then conversion coated still passed 336 hours salt spray as well as all painted adhesion and corrosion resistance tests. Incidentally, the copper content of the etch/cleaner bath actually dropped slightly while parts were being processed.

A one-year production trial of this process was conducted at Sure Power Industries, Tualatin, OR, with consistently passing results and no bath failures. The aluminum level of that 1200 gallon production bath rose to about 1100 ppm, then leveled off (see *Figure 8*). A small amount of aluminum fluoride sludge formed near the end of the trial. No panel or part failures were experienced throughout the trial. A metal analysis of the production baths is shown in *Table 4*, and again shows very little heavy metal buildup in either bath. The parts processed through this bath were a mixture of 5052, 6061, and 2024 alloys.

A list of some of the aerospace companies who have successfully tested this process is shown in *Figure 9*. Recently, The Boeing Co. issued a Process Specification Departure for its BAC 5765 Specification for Deoxidizing of Aluminum. This PSD allows the use of this system for heavy duty deoxidizing prior to conversion coating, anodizing, and many other operations.

Asko Processing, Inc., of Seattle, WA, has confirmed the viability of using this deoxidizing system prior to welding. They have reported that parts deoxidized in this system maintain low surface resistance longer than parts deoxidized with chromated deoxidizers.

Before we conclude our presentation, let's take a look at where we see conversion coating processing is going in the foreseeable future. In doing so, we will also address the concerns of some about the use of a <u>two</u> step deoxidizer system. *Figure 10* shows the procedure which we have recommended for the past 40 or so years. Note the solvent vapor degrease, alkaline cleaner containing phosphates, chromated deoxidizer and conversion coating baths. Every one of these processes today represents an environmental problem.

In the very near future our recommended process for commercial and military aerospace will be the process shown in *Figure 11*. Here we have an environmentally safe aqueous degreaser, a two-step environmentally safe deoxidizer, and an environmentally safe conversion coating.Look at the number of steps: except for a rinse after the degreaser, the number of steps is the same.These two charts do not show the waste treatment facilities required for each process. The process of the 90's will require a much smaller waste treatment facility and drastically less sludge to dispose of, and the sludge will no longer be extremely hazardous- a sizable premium for an extra rinse tank.

Conclusion

A non-chromium, non-heavy metal,non-ferricyanide deoxidizing system is now commercially available which equals, and in some cases surpasses, the performance of chromated deoxidizers. Laboratory and production line test results have confirmed that the system contributes to the conformance of a good quality chromate conversion coating to the applicable military and aerospace specifications, even on alloys which present finishing difficulties. It has been approved for use by the Boeing Company and other aerospace companies.

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17. The Boeing Co., Seattle, WA, *Boeing Material Specification BMS 10-11, Rev. U, Chemical and Solvent Resistant Finish*, **Oct. 28, 1991**.

FIGURE 1

Deoxidizer Chronology

1950- Present

- 1950- Chromated Deoxidizers Formulated
- 1963- Ferric Sulfate Deoxidizer Patented
- 1970- Ferricyanide in Chromated Deoxidizers Patented
- 1984- Batiuk Non-Chrome 2-Step Process Patented
- 1991- McMillen Non-Chrome 2-Step Process Patented

FIGURE 2

Deoxidizing vs. Desmutting

- Deoxidizing- The removal of oxides and other inorganics which would interfere with normal finishing procedures.
- Desmutting- The removal of pretreatment residues without significant attack on aluminum.

FIGURE 3

DEOXIDIZER APPLICATIONS*

Heavy Duty Deoxidizing

- Removal of Heavy Oxides
- Removal of Corrosion Products
- Removal of Heat Treat Discoloration
- After Abrasive Cleaning
- After Shotpeening
- Prior to Penetrant Inspection
- Prior to Conversion Coat
- Prior to Anodize
- Prior to Chem Milling

* From Boeing BAC 5765

FIGURE 4

DEOXIDIZER APPLICATIONS*

CONTINUED

- Light Duty Deoxidizing
  - When Heavy Oxides, Corrosion, Etc. Not Present
- Removal of Smut
- Preparation of Surfaces for Resistance Welding
- Preparation of Surfaces for Fusion Welding
- Preparation of Surfaces for Brazing
- Preparation of Surfaces for Adhesive Bonding
- Removal of Foreign Metal Contamination
- Removal of Flux
- "Skin Quality" Deoxidizing
  - Prior To Clear Conversion Coat

* From Boeing BAC 5765

TABLE 1. Auger Analysis
Cleaned and Deoxidized 2024-T3 Panels
Per Cent Atomic Concentration

Sample Number	Depth, Å	Si	C	Ca	O	Cr	F	Cu	Mg	Al
1	0	2.7	4.3	6.1	31.8	-	-	-	32.3	22.8
1	30	2.3	2.0	1.7	36.7	-	-	-	33.0	24.3
2	0	-	8.0	-	38.5	-	3.8	11.6	-	36.8
2	30	-	2.5	-	30.5	-	1.5	21.8	-	43.6
3	0	-	6.4	-	40.4	a	9.1	7.3	-	35.9
3	30	-	2.6	-	35.3	a	4.0	14.3	-	43.7

Sample Identification

☐ #1=Cleaned Only ☐ #2=Non-Cr Deoxidized ☐ #3=Chromate Deoxidized

a- present but not quantified

TABLE 2. Deoxidizer Loading
Aluminum and Copper Levels

	Acid Cleaner	Desmut
Aluminum	1200 ppm	90 ppm
Copper	<5 ppm	64 ppm

Baths Loaded with Bare 2024-T3
18 Sq. Ft./Gal. Processed

TABLE 3. Deoxidizer Loading

Acid Etch/Cleaner Bath Doped with $CuSO_4$

Copper Level

	Acid Cleaner	Desmut
Initial	480 ppm	<5 ppm
Final	430 ppm	260 ppm

Processed Bare 2024-T3 Panels
Panels Conversion Coated after Deoxidizing
All Passed 336 Hours Salt Spray, Paint Adhesion Tests

FIGURE 5. Process Control

Deoxidizer System

- Acid Etch/Cleaner
  - Acid Titration
  - Fluoride Probe
  - Temperature
  - Etch Rate
- Desmut
  - Acid Titration
  - Oxidizer Titration

FIGURE 6. Unpainted Performance Tests

2024-T3, 6061-T6, 7075-T6 Panels (All Passing)*

- ✓ Uniform Appearance
- ✓ 168 Hours Salt Spray (Commercial)
- ✓ 336 Hours Salt Spray (Military)
- ✓ Intergranular Attack
- ✓ End Grain Pitting

* All Panels Non-Cr Deoxidized + Chromate Conversion Coated

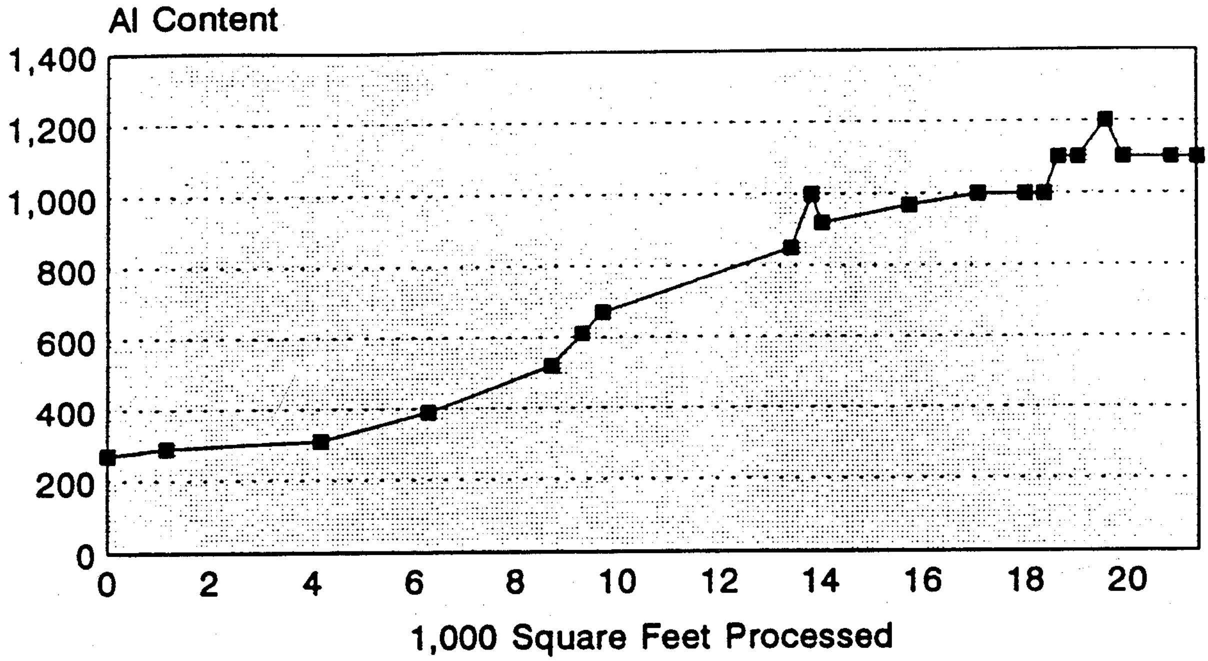
FIGURE 7. Painted Performance Tests

Bare 2024-T3 Panels* (All Passing)

- ✓ Dry Adhesion
- ✓ Wet Adhesion
  - 7-Day Water Immersion + Adhesion
- ✓ Humidity + Adhesion
  - 30 Days @ 120° F +100% R. H.
- ✓ Salt Spray
  - 3000 Hours per ASTM B-117

*Primed Only and Top-Coated Panels
Following Non-Cr Deoxidize + Chromate Conversion Coat
BMS 10-11U Paints

FIGURE 8. Acid Etch/Cleaner
Aluminum Dissolution



Production Bath

TABLE 4. Deoxidizer Loading
Metals in Solution (ppm)
ICP Analysis

	Acid Cleaner	Desmut
Aluminum	1100	57
Copper	<5	4
Iron	8	7
Magnesium	9	2
Chromium	5	7

Production Bath- 21,350 Sq. Ft. Processed
Mixed Alloys: 5052, 6061, 2024

FIGURE 9

Non-Chrome Deoxidizer

Cooperative Evaluators

- The Boeing Co.
- McDonnell Douglas
- Grumman Aircraft
- Northrop
- Rohr
- Sure Power Corporation
- Asko Processing, Inc.

FIGURE 10

Chromate Conversion Coat Process

1950- 1993

1. Vapor Degrease

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2. Alkaline Clean
3. Rinse
4. Chromated Deoxidize
5. Rinse
6. Chromate Conversion Coat
7. Rinse
8. Air Dry ($\leq$120°F)

FIGURE 11

Non-Chromium Conversion Coat Process

1993 and Beyond

1. Aqueous Degrease
2. Rinse

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3. Acid Etch/Clean
4. Rinse
5. Desmut
6. Rinse
7. Non-Chrome Conversion Coat
8. Rinse
9. Air Dry