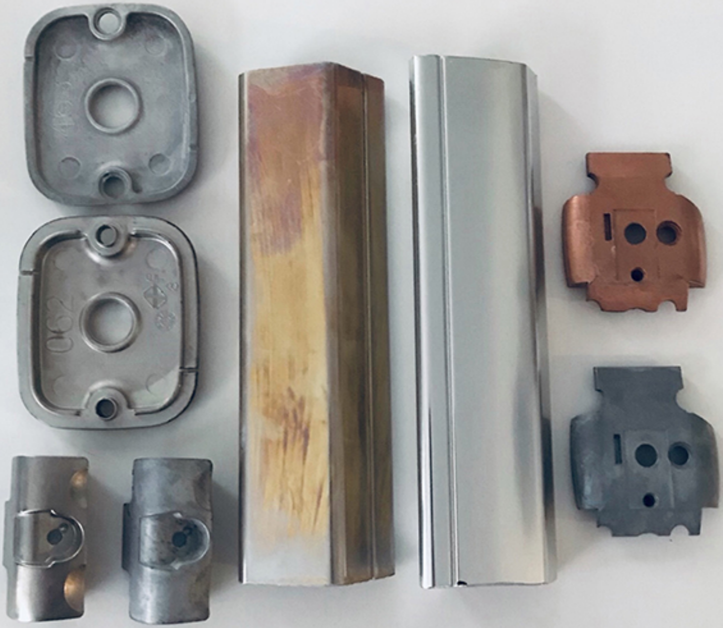
Conversion Coatings



John W. Bibber

Conversion Coatings

Conversion Coatings

By

John W. Bibber

Cambridge
Scholars
Publishing

Conversion Coatings

By John W. Bibber

This book first published 2019

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-5275-3850-8
ISBN (13): 978-1-5275-3850-4

TABLE OF CONTENTS

INTRODUCTION

The expression "conversion coating", as used in the metal finishing industry, refers to the conversion of a metal surface to one that will more easily accept applied coatings (e.g., commercial paints or plated metal) and/or be more corrosion resistant. In all cases, a purely chemical process of one kind or another generates the coating in question. Conversion coatings are rather thin (not over 6000nm thick), quickly and easily formed, easily scratched and, if used to enhance adhesion, are generally coated shortly after being formed to prevent degradation.

The most important part of the entire conversion coating process is cleaning the metal and removing any unwanted oxides; this is known as the “deoxidization” of the metal. The cleaning process and the “deoxidization” may be considered the essential part of conversion coating in that it is chemically modifying the surface of the metal and, if not properly executed, may actually prevent the formation of the desired conversion coating. This process can also enhance the properties of the conversion coating you are trying to produce; due to this fact, I have provided a large section on the cleaning of both light and heavy metals.

In chemistry, light elements are considered to have a density of no more than five and the majority of conversion activity takes place using light metals, such as aluminum and magnesium. Amongst the heavy metals, iron and its alloys always receive the most attention. The most widely used conversion coatings systems have been chromium based, due to their good corrosion resistance; phosphate based for good paint adhesion; various organic or inorganic polymer-based systems; and heavy metal systems used in conjunction with phosphates in one form or another.

CHAPTER 1

THE LIGHT METALS

There has been some dispute in the scientific community over what constitutes "light metals". Engineers claim that only the metals with a density no greater than three should be considered "light". In chemistry, light metals have a density no greater than five. This takes us up to titanium on the periodic chart, which has a density of about 4.5 grams per cc.

All the elements that easily lose electrons are referred to as metals. That is to say, metals want to oxidize and light metals, in particular, really want to oxidize. As a consequence, light metals are quite easily conversion coated and, therefore, they are frequently used in industrial conversion coating.

The first of the light metals is lithium, which has a density of only 0.5 grams per cc. It has the greatest tendency to lose electrons (oxidize) and will easily catch on fire and is even able to burn in a nitrogen atmosphere. By itself, it has little use, if any, in the metal finishing industry but has been used as an alloying element in aluminum and other light elements in the aerospace industry.

Beryllium is next in this series of light metals with a density of about 1.85 grams per cc and the highest melting point at 1287° C. At an ambient temperature, it resists oxidation, has excellent thermal conductivity, poor ductility, and its salts are very poisonous. There is little use for the pure metal, with the exception of the aerospace industry, as a result of its high melting point and lightness.

Sodium follows with a density of about 0.97 grams per cc. It is very easily oxidized, soft and easily cut, and is only used in the metal finishing industry to reduce (deoxidize) other metals.

Next in the series is magnesium with a density of about 1.74 grams per cc and a melting point of 650° C. This is the second most widely used member of the light elements. It is easily oxidized, but not to the extent of sodium or lithium and, unlike beryllium, has no poisonous salts. In addition, it has a tensile strength of about 33.000 psi., making it the lightest of the structural metals. It is used extensively in many applications, but must have a good corrosion resistant conversion coating due to its risk of oxidation.

Aluminum comes next; this is the most widely used of the light elements. It has a melting point of 660.4° C., making it easy to cast; a density of about 2.7 grams per cc.; and a tensile strength of about 30,000 psi. It is currently the most widely used of the light metals in industry and has numerous alloys associated with it, all of which are conversion coated for one reason or another and, as such, will be discussed to a greater extent than any other of the metals.

Potassium and calcium follow, but have little use in the metal finishing industry as they are very soft and will easily ignite. They are used as deoxidizing agents for other metals and in the separation of titanium from its ore. Potassium has a density of about 0.86 grams per cc. and a melting point of 63.3° C., while calcium has a density of 1.54 grams per cc. and a melting point of 842° C.

Scandium is the next and would probably be widely used as a structural metal if not for the fact that it is quite rare. Its melting point is 1541° C. It has a density of about 2.99 grams per cc.

Titanium is the last element in the light metal series, with a density of about 4.5 grams per cc. and a melting point of 1668° C. It is quite widely used in aerospace applications, as it is as strong as mild steel with only 45% of its weight. The separation of titanium from its ores is a rather long, involved, and expensive process and, as a result, it is not as widely used industrially as aluminum or magnesium.

Light Metal Alloys and Their Properties

Aluminum:

Aluminum, followed by magnesium, is by far the most widely used of the light metals. A discussion of their alloys, associated properties, and general chemical composition will follow. In North America, the Aluminum Association Inc. is responsible for the allocation and registration of aluminum alloys. At present, there are over 400 wrought aluminum alloys and over 200 aluminum alloys in the form of ingots and castings registered. The alloy chemical composition limits for all of these registered alloys are contained in the Aluminum Association's publications entitled "International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys" and "Designations and Chemical Composition Limits for Aluminum Alloys in the Form of Castings and Ingot". These are quite useful to the welding engineer when developing welding processes or when considering the chemistry of the alloys and its association with crack sensitivity. Aluminum alloys are organized into a number of groups, based on their characteristics, such as mechanical and thermal responses, or thermal and mechanical treatment, as well as the primary alloying element added. When we consider the identification/numbering identification system used for aluminum alloys, the above characteristics are identified. The cast and wrought aluminum alloys have different systems of identification: cast has a 3-digit system and 1-decimal place system; wrought has a 4-digit system.

Wrought Alloy Series	**Principal Alloying Element**
1000	99.000% Minimum Aluminum
2000	Copper
3000	Manganese
4000	Silicon
5000	Magnesium
6000	Magnesium and Silicon
7000	Zinc
8000	With the exception of one member of the series, all of the alloys contain iron

The second single digit (xXxx), if different from 0, shows the modification of the alloy in question. The third and fourth digits (xxXX) are arbitrary numbers that identify a specific alloy in the series. For example, in the alloy 2124, the number 2 indicates that it is from the copper alloy series; the 1 shows that it is the first change to the original alloy; and the 24 identifies the change in the 2xxx series. The only exception to this system is the 1xxx series aluminum alloys in which case the last 2 digits provide the minimum aluminum percentage above 99%: for example, 1060 (99.60% minimum aluminum).

Cast Alloy Designation

The cast alloy designation system is based on a 3 digit-plus decimal designation xxx.x (e.g., 383.0). The first digit (Xxx.x) indicates the principal alloying element added to the aluminum alloy.

Cast Aluminum Alloy Designation System

Alloy Series	Principal Alloying Element
100.0	99.000% minimum Aluminum
200.0	Copper
300.0	Silicon Plus Copper and/or Magnesium
400.0	Silicon
500.0	Magnesium
600.0	Unused Series
700.0	Zinc
800.0	Tin

The second and third digits (xXX.x) are arbitrary numbers used to identify a specific alloy in the series. The number following the decimal point indicates whether the alloy is a casting (.0) or an ingot (.1 or .2). A capital letter prefix indicates a modification to a specific alloy.

Example: Alloy, A383.0: The capital A (Axxx.x) indicates a modification of alloy 383.0. The number 3 (A3xx.x) indicates that it is from the silicon plus copper and/or magnesium series. The 83 (Ax83.0) identifies the alloy within the 3xx.x series, and the .0 (Axxx.0) indicates that it is a casting and not an ingot or relative pure metal ready for further processing. The chemical composition of cast aluminum alloys manufactured in the U.S. are indicated below. There similar are designation systems used in other countries, but these are the most generally accepted and internationally used all. In addition, the chemical compositions of the castings differ little from one country to another.

Designation	Si, %	Cu, %	Mn, %	Mg, %	Zn, %	Ti, %	Others, %
201.0	0.1 max.	4.0–5.2	0.2–0.5	0.15–0.55	-	0.15–0.35	Ag 0.4–1.0
208.0	2.5–3.5	3.5–4.5	0.5 max.	0.1 max.	1.0 max.	0.25 max.	-
222.0	2.0 max.	9.2–10.7	0.5 max.	0.15–0.35	0.8 max.	0.25 max.	-
333.0	8.0–10.0	3.0–4.0	0.5 max.	0.05–0.5	1.0 max.	0.25 max.	-
356.0	6.5–7.5	0.25 max.	0.35 max.	0.2–0.45	0.35 max.	0.25 max.	-
413.0	11.0–13.0	1.0 max.	0.35 max.	0.1 max.	0.5 max.	-	-
443.0	4.5–6.0	0.6 max.	0.5 max.	0.05 max.	0.5 max.	0.25 max.	-
514.0	0.35 max.	0.15 max.	0.35 max.	3.5–4.5	0.15 max.	0.25 max.	-
518.0	0.35 max.	0.25 max.	0.35 max.	7.5–8.5	0.15 max.	-	-
705.0	0.2 max.	0.20 max.	0.4–0.6	1.4–1.8	2.7-3.3	0.25 max.	Cr 0.2–0.4
713.0	0.25 max.	0.4–1.0	0.6 max.	0.2–0.5	7.0–8.0	0.25 max.	-
852.0	0.4 max.	1.7–2.3	0.1 max.	0.6–0.9	-	0.25 max.	Sn 5.5–7.0, Ni 0.9–1.5

Characteristics of the Cast Aluminum Alloys

200.0 Series: High strength
Low corrosion resistance
Susceptible to stress (corrosion cracking)
Low ductility
Susceptible to heat stress cracking
300.0 Series: High Strength
Low ductility
Good ware resistance
Good corrosion resistance in the absence of copper
Good machinability
400.0 Series: Moderate strength
Moderate ductility
Good wear resistance
Easily cast
Excellent corrosion resistance
500.0 Series: High corrosion resistance
Good machinability
Good cast alloy for anodizing
700.0 Series: Good dimensional stability
Good corrosion resistance
Poor casting properties
Good machinability in copper containing castings
800.0 Series: Low strength
Good ware resistance
Good machinability

The Wrought Aluminum Temper Designations

As we look at the different types of aluminum alloys, we can see that there are a large number of differences in their characteristics and, therefore, their end use application. The first point to recognize is that there are two distinctly different types of aluminum within the series mentioned above. These are the heat treatable aluminum alloys (those able to gain strength through the addition of heat) and the non-heat treatable aluminum alloys. This is particularly important when considering the effects of welding on these two types of aluminum alloys.

The 5xxx, 3xxx, and 1xxx series aluminum alloys are non-heat treatable and only use strain hardening. The 7xxx, 6xxx, and 2xxx series aluminum alloys are heat treatable and the 4xxx series may be heat treatable and non-heat treatable alloys. The 7xx.x, 4xx.x, 3xx.x and 2xx.x series cast alloys are heat treatable. Strain hardening is not generally applied to castings.

The heat treatable alloys obtain their best mechanical properties through the process of thermal treatments; solution heat treatment and artificial aging are the most frequently used. Solution heat treatment is the process of heating the alloy to an elevated temperature (around 980–1000 Deg. F) in order to place the alloying elements or compounds into a solution. This is followed by quenching, usually in water, to give a supersaturated solution at room temperature. Solution heat treatment is generally followed by the aging process or the precipitation of a portion of the elements or compounds from a supersaturated solution in order to yield desirable properties. The aging process is divided into two types: aging at elevated temperatures (artificial aging) or aging at room temperature (natural aging). Artificial aging temperatures are typically about 310–330 Deg. F. A number of heat treatable aluminum alloys are used for welding fabrication in their solution heat treated and artificially aged condition. The non-heat treatable alloys obtain their best mechanical properties through strain hardening, which is the process of improving strength through the application of cold working. The temper designation system addresses the alloy's condition, which is known as tempers. The temper designation system is an extension of the alloy numbering system and is a series of letters and numbers which follow the alloy designation number and are connected by a hyphen. For examples, 7075-T6, 2024-T3, 6061-T6, 5454-H32, and 4032-T6.

Examples of Temper Designations

Letter	
F	As fabricated: In other words, products of a forming process in which no special control over thermal or strain hardening conditions is used.
O	Annealed: Products which have been heated to produce the lowest possible strength condition to improve ductility.

H	Strain hardened: Products that are strengthened through cold-working. Strain hardening may be followed by supplementary heat treatment, which produces a reduction in strength. The “H” is always followed by two or more digits.
W	Solution heat-treated: An unstable temper that only applies to alloys that age spontaneously at room temperature after solution heat-treatment.
T	Thermally treated: To give stable tempers other than H, O, or F. Applies to products which have been heat-treated with supplementary strain-hardening to produce a stable temper. The “T” is always followed by one or more digits.

Wrought Aluminum Alloys and their Characteristics

1000 Series Alloys: This series is generally known as the pure aluminum series, as the alloys are required to have a minimum of 99.0% aluminum. They may be welded but, as a result of their narrow melting range, this is difficult. These alloys are generally selected due to their superior corrosion resistance, such as in specialized chemical pipping and tanks, or for their good electrical conductivity, such as in bus bar applications. These alloys have relatively poor mechanical properties and are not often used for general structural applications (ultimate tensile strength of between 10 to 27 ksi). The base alloys are often welded with matching filler alloys or with 4xxx filler alloys depending upon on the specific application and performance requirements. With the use of a hard vacuum, 1000 series aluminum may evaporate as a vapor and be deposited on glass as a reflective film for telescope mirrors, steel for aerospace applications, or on various plastics in a decorative application. Pure silicon dioxide may then be heated and vacuum evaporated onto the "vapor deposited aluminum" to provide corrosion protection in aerospace applications or telescopes.

2000 Series Alloys: 2000 series aluminum/copper alloys are used for their high strength and performance in aerospace applications, as they have an ultimate tensile strength of 27 to 62 ksi. They are often used for various aerospace and aircraft applications. They have excellent strength over a wide range of temperatures. Some of the 2000 series alloys have been branded as "non-weldable" in arc welding processes because of their susceptibility to hot and stress corrosion cracking. However, this has a lot has to do with the type of arc welding used and the expertise of the welder. The base alloys are often welded with high strength 2xxx series filler alloys designed to match their performance, but may be welded with 4xxx series fillers containing silicon or silicon and copper; this is dependent on the application and service requirements. In any event, these alloys are very easily corroded unless coated with a thin protective film of "1000" series (pure aluminum) alloy, conversion coated with a chromate-based conversion coating (which is difficult as chromates are known cancer causing agents), or conversion coated with one of several permanganate-based conversion coating systems.[1]

3000 Series Alloys: These aluminum/manganese alloys are of moderate strength, have good corrosion resistance, good formability, and work well at high temperatures. As a result, one of their first uses was in frying pans. Heat resistance comes primarily from the manganese, but you cannot add more than about 1.5%. They are also used for heat exchangers in air conditioners and power plants. Their moderate strength precludes their consideration for structural applications. These base alloys are welded with 4xxx, 5xxx, and 1xxx series filler alloys, depending on their specific chemistry, application, and service requirements. Various organic based conversion coating systems (amine phosphates) may be used to prevent staining the 3000 series alloys due to boiling water or wet and humid conditions.

4000 Series Alloys: These are aluminum/silicon alloys (silicon additions ranging from 0.6 to 21.5%), where silicon is intentionally added to produce a low melting and free flowing alloy for the sole purpose of being able to weld aluminum. These characteristics are desirable for filler materials used for both fusion welding and brazing. A number of these alloys have been designed to have additions of magnesium or copper, which provides them with the ability to respond favorably to solution heat treatment and to improve upon the weldability of various alloys. Typically, these heat treatable alloys are only used when a welded component is to be subjected to post-weld thermal treatments. The vast majority of the "4000" series alloys in general use have a rather high silicon content and, as such, become dark gray or black when oxidized (anodized) or conversion coated which may or may not be desirable.

---

[1] Spadafora, S.J. 1992. "Naval Air Warfare Center Aircraft Division Warminster", Pa., Report No. NADC-92077-60

5000 Series Alloys: These aluminum/magnesium alloys (magnesium additions ranging from 0.2 to 6.2%) have the highest strength of the non-heat treatable alloys and, as such, are often used as armor plate in military applications. In addition, this alloy series is readily weldable and, for that reason, they are used for a wide variety of applications, such as shipbuilding, transportation, pressure vessels, bridges, and buildings. Magnesium base alloys are often welded with filler alloys, which are selected after considering the magnesium content of the base material, as well as the application and service conditions of the welded component. Alloys in this series with more than 3.0% magnesium are not recommended for elevated temperature service above 150° F because there may be sensitization and susceptibility to stress corrosion cracking. Base alloys with less than approximately 2.5% magnesium are often welded successfully with "4000" or "5000" series filler alloys. The most commonly used alloy from the "5000" series is 5052, which is generally recognized as the maximum magnesium content base alloy that can be welded with a "4000" series filler alloy. Due to the problems associated with eutectic melting and associated poor as-welded mechanical properties, it is not recommended to weld other alloys from this series that contain higher amounts of magnesium. The higher magnesium base alloys are only welded with "5000" filler alloys which, as a general rule, match the base alloy composition.

6000 Series Alloys: These are the aluminum/magnesium-silicon alloys with about 1.0% magnesium and silicon. They are found widely throughout the welding fabrication industry, generally used in the form of extrusions, and often found in many structural components. The addition of magnesium and silicon to aluminum produces a compound called magnesium-silicide, which gives these alloys the ability to become solution heat treated and, as a result, greatly increase their strength. These alloys have the tendency to crack and, for this reason, they should not be arc welded without a filler alloy. The addition of enough alloy material during the arc welding process is essential in order to give the necessary dilution to the base alloy and thus prevent a hot cracking problem. They are welded with both "4000" and "5000" filler alloys, depending upon the application and service requirements needed.

7000 Series Alloys: These are aluminum/zinc alloys and, as a result of the zinc component, they are some of the highest strength aluminum alloys available. These alloys are generally used in high performance aircraft and aerospace applications. Like the "2000" series alloys, they also include alloys that are not good candidates for arc welding, and others that are often arc welded successfully. The more commonly welded alloys of this series, such as 7005, are generally welded with the "5000" series alloys.

8000 Series Alloys: The "8000" series alloys are similar to the "1000" series in terms of their properties, but are generally much stronger and stiffer than any of the "1000" series aluminum alloys. This is because most are alloyed with iron. The exception is 8090, which is alloyed with lithium and used in aerospace applications. One problem with the 8090 alloy is that the lithium atom is small enough to "cooked" out of the alloy. See ASTM Specification: B800-05, Standard Specification for 8000 series Alloy Wire for Electrical Purpose Annealed and Intermediate Tempers for more conductivity data.

Magnesium Alloys: Magnesium alloys, in the United States of America, are designated according to ASTM specification B275: "Codification of Certain Metals and Alloys". The naming system is unusual in that the designation system actually describes the primary alloying elements and their average percentage content. The following is a list of the alloy element codes:

A Aluminum
B Bismuth
C Copper
D Cadmium
E Rare Earths
F Iron
G Magnesium
H Thorium
J Strontium
K Zirconium
L Lithium
M Manganese
N Nickel
P Lead
Q Silver
R Chromium
S Silicon
T Tin
V Gadolinium
W Yttrium
X Calcium
Y Antimony
Z Zinc

As an example, in the magnesium alloy, AZ91D, the "A" stands for aluminum and "Z" stands for zinc. The 9 indicates that the percentage of aluminum present in the alloy is the average rounded aluminum percentage between 8.6 and 9.4. Zinc, the second letter, represents 1 % or the average rounded zinc percentage between 0.6 and 1.4, and the letter "D", as the final letter, represents that this is the fourth (A, B, C, D) alloy, which has an "AZ91" designation, but with not enough of a change in composition to require a new designation. In other words, it has less than 1 % of an increase in alloy composition in terms of rounded off percentages.

The ASTM specification B296-03: Standard Practice for Temper Designations of Magnesium Alloys, Cast and Wrought directly follows ASTM specification B275. Unlike the differences in the naming systems between that of aluminum and magnesium, the system used to designate tempers and so on is much the same.

Due to the fact that magnesium is about one third lighter then aluminum and has about the same tensile strength, a lot of research has been performed in an effort to replace aluminum in many applications. Since about 2003, a lot of work has been put into producing wrought magnesium, but cast magnesium alloys are still used to much greater extent than wrought alloys. This is because magnesium has a crystal structure (referred to as hexagonal) that results in magnesium laying down in flat, stiff sheets. This is a result of the magnesium atoms' small size and the resulting strong forces of attraction and repulsion between them. This makes it brittle and trying to bend a sheet of magnesium will just cause it to break in two. Aluminum has a body centered cubic arrangement of the atoms which is more open and, as a result, may be more easily deformed or "bent". This also explains why most magnesium alloys contain aluminum. The aluminum gets rid of a lot of the "stiffness" by providing the magnesium with more space to move around. Magnesium has 12 near neighbors in its crystal structure, while aluminum has 8. Aluminum is a smaller atom than magnesium. The most commonly manufactured cast magnesium alloys are listed below. You will note "Elektron 21", which was named by "Magnesium Elektron, Ltd.". This is a British company that produce a wide range of magnesium alloys, many of which contain rare earth elements that, more than anything else, impart a great deal of inertness to improve the corrosion resistance of the alloy and allow it to be easily machined. Magnesium has a density of 1.738 grams per cubic centimeter, while most of its alloys have a density of about 1.8 grams per cubic centimeter.

AM50
AM60
AZ81
AZ63
AZ91
HK31
ZC63
ZE41
ZK61
ZK51
WE43

WE54
QH21
QE22
HZ32
Elektron 21

Research continues on the production of more useful wrought magnesium alloys but, to date, most wrought alloys continue to have aluminum, zinc, and rare earth as their primary alloying elements to provide more corrosion resistant alloys and, in some cases, improvements in structural strength.

CHAPTER 2

THE CLEANING AND DEOXIDATION OF LIGHT AND HEAVY METALS

In any metal cleaning process, you want to remove the loose surface dirt and any metal working fluids or lubricants without excessive pitting or oxidation in the metal being cleaned; this is because you will do little more than "dig up" more soil to be cleaned off in the form of various metal oxides. The four most widely used light metals, from most to least, are aluminum, magnesium, titanium, and beryllium. In all cases, it is very difficult to "clean" these metals without leaving behind some kind of oxide film on the surface. This is due to the fact that they are all quite easily oxidized, but the conversion process will remove and, to some extent, include these oxides in the conversion coating you are forming.

The expression "deoxidation" is used in the metal finishing industry to mean the removal of unwanted metal oxides left after the cleaning process. This generally entails the use of one or more acid dips or, in some cases, the use of a strong alkaline solution. An acid-based cleaner may be added to an acid-based "deoxidizer" to allow for cleaning and deoxidation to take place in one step.

At one point in time, the only "metal working fluids" in use were animal fats and other naturally occurring oils and fats. Today, almost all metal working fluids are synthetic and contain amine-based products that will only come off with acid-based cleaners.

Aluminum and Iron and their Alloys

Of all the light metals, aluminum and its alloys are more frequently used and conversion coated than any other of the light metals. As a result, most of the cleaning methods outlined below are related to the deoxidization of aluminum and/or iron and its alloys. This is because iron is the most commonly used and conversion coated heavy metal. When cleaning aluminum or iron, or for that matter any metal, you are actually generating

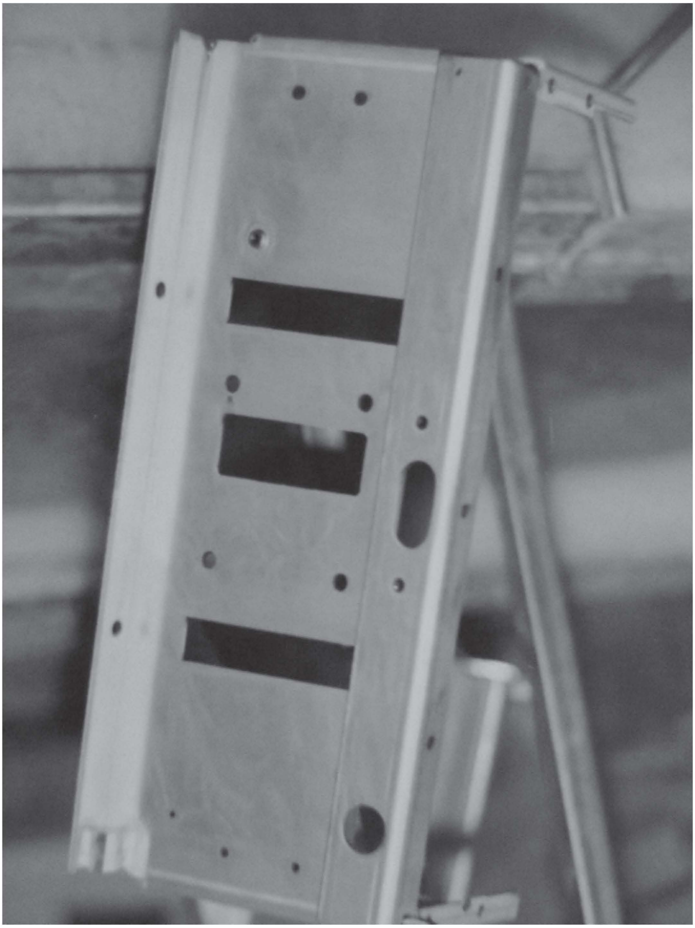


Figure 2.1: Aluminum surface cleaned too strongly and then conversion coated.

a "conversion coating" by "converting the surface of the metal by chemical means into a surface that will more easily accept applied coatings or improve upon the corrosion resistance of the metal being processed". The cleaning process may be designed to intentionally generate more metal oxides, strip off all the oxides, or leave a thin film of organic material to retard the formation of metal oxides during periods when the metal is exposed to oxygen or rinse water, depending upon the alloy you are working with and the type of cleaner you are using. How "clean" a given piece of metal needs to be will depend upon how much you want to spend in the cleaning process. Having said that, we can also say that the most important part of any secondary conversion coating process will depend upon having the metal cleaned so that the conversion coating will function as designed.

Figure 2.2: Aluminum surface cleaned too strongly and then activated with a strong alkali and conversion coated.

Water does not really lay down well on any given surface. Water wants to cling to itself in the form of small droplets. Soap pulls the water away from itself, so that it becomes attached to the soap instead. This makes it much easier for the water to attach itself (along with the soap) to the article being cleaned. Loose particles of dirt or organic fluids attach themselves to the soap and are then rinsed off. Any or all of the attached organics, must first be converted into a liquid form by heat or the use of solvents in order for them to be attracted to the soap and removed in the rinsing process.

Vapor degreasing

As a result of more strict environmental regulations on the use of solvents in general, just about the only safe way to solvent degrease is by using vapor degreasing equipment. Increasingly, the solvent of choice will be a rather expensive selection of fluorocarbon solvents or N-propyl bromide which is, at the moment, the solvent of choice in most vapor degreasing.

With vapor degreasing, the part being cleaned is placed into a chamber that is saturated with the vapors of an organic solvent that is suitable for dissolving the organics attached to the article. As the article is cooler than the organic solvent, the solvent condenses on the article, dissolves or flushes away the organics, condenses and drips down to be used over and over again. Therefore, the article is constantly being flushed with pure solvent. Some of the soils will not be soluble in the solvent and you will always have an oily residue on the article, thereby making it all but impossible to prevent some solvent from getting out into the open air. This of course requires ventilation and its associated costs.

The cooler the parts and the greater the efficacy of the degreaser's cooling system, the faster fresh solvent pours over the articles to be cleaned. The articles should be arranged to avoid the lower layers from condensing the vapors before they are able to reach the upper layers. Vapor degreasers, if operated properly, will effectively remove heavy mineral oils, viscous or polymerized oil-based cutting lubricants, and high molecular mass chlorinated oils used as lubricants and waxes. These materials are quite difficult to remove and will only come off with a vapor degreaser. Vapor degreasers will not dissolve water soluble organics like soap or glycerin. Vapor degreasing will remove most, if not all, buffing compounds constructed with high melting waxes.

The condensing vapors will not provide much in the way of agitation; therefore, insoluble residues are generally not removed. This may be a larger problem than you think, particularly if you have very fine soil mixed with oil. The fine particles left behind will adhere to the article being cleaned. In many cases, degreasers will have a cold or warm spray stage, which is followed by a condensed vapor flush. For small parts that cannot easily be sprayed, they may be processed in an immersion stage with a warm or cool solvent. In some cases, a degreaser will have a boiling solvent stage followed by a cool solvent stage. Combinations of such stages may also be used with an ultrasonic cleaning stage for tough cleaning problems.

The vapor degreaser needs to be located away from any drafts of air which will blowing away any solvent vapors before they can condense with cooling. At the same time, there must be enough air circulation to prevent an accumulation of the vapors. Water must be excluded from the degreaser, as this would generate hydrogen bromide in the case of n- propyl bromide, or hydrogen chloride, in the case of chlorinated hydrocarbons, when in contact with hot aluminum. Do not use unstabilized solvent. If acid is generated, the machine must be drained and rinsed out with an alkaline wash, such as sodium carbonate, then rinsed free of the alkaline solution and dried.[1]

Emulsion Cleaning

Emulsion cleaning is nothing more than a solvent being dispersed in water with various soaps. As a result, most of the soap is not available to clean the soil off of a soiled aluminum article. This is taken care of by the solvent being used. The solvent is able to break up solid particles on the soiled article in question at an ambient temperature. Emulsion cleaners do not react with the aluminum in any way. As in the case of vapor degreasing, they are very flexible in the type of solvent that may be used. There are three methods that are generally used in emulsion cleaning. In one method, the cleaning fluid will be in two or more phases. One phase consists of a water solution containing the emulsion forming agents (wetting agents, water soluble amines, etc.). The other phase consists of the various organics, none of which should have a flash point above 100° F. or 38° C. The other organics consist of light oils and/or various waxes dissolved in a solvent, which may have a flash point below 100° F. As the article to be cleaned is placed into the solutions it will first come into contact with the organics and then the water phase. The organics either dissolve some or all of the organics, or break up the attached organics into easily emulsified particles. The water phase then emulsifies the organics and wets out the aluminum. An example of this is triethanolamine, which is quite soluble in water and various fatty acids that are dissolved in the organic solvent. The triethanolamine then reacts with the fatty acids (oleic acid, lauric acid, etc.) to generate a soap; this is then able to emulsify some or all of the organics detached from the aluminum by the solvent.

In another method, two stages are used. The article to be cleaned is first dipped (dipping being the best procedure as the entire article is exposed to the solvent) or sprayed down with a non-water soluble organic solvent. This solvent contains various fatty acids that will be converted into soap once the article is placed into the water solution of one or more water-soluble alcohol-based amines. As the article is placed in the water-amine solution a white milky film will be formed on the article which is then rinsed off. The cleaning actually takes place in the rinse part of the process but, in many

---

[1] Spring, S. Industrial Cleaning. 1974. Prism Press, Melbourne, AU

cases, the article being cleaned will go from the rinse tank into an alkaline cleaning tank to remove other soils still attached to the article.

The third process is to use the first process with a pressure spray or rotary-tumbler type of mechanical washing machine. Depending upon the type of organics being used, the temperature range should be from 50° C. (122° F.) to about 70° C. (158° F.). Some sources mention the use of temperatures up to 90° C. (194° F.) but, at that temperature, you will start to form an oxide film on the aluminum which will trap and hold soil. In all cases of emulsion "cleaning" there will still be a film of dirt on the aluminum that must be removed by some kind of attack on the aluminum itself (see acid and alkaline cleaning).

Acid Cleaning and Oxide Removal

With amine-based metal working fluids impressed into a given piece of metal, you must use an acid-based soap to remove them, use the "brute force" of a strong acid that will oxidize the metal working fluids, or dissolve away enough metal to allow the metal working fluids to escape out into your acid bath. The acids available for use are as follows:

1. Sulfuric acid: This is the most widely used of the strong mineral acids and, as a result, the least expensive. It is available as a 95% to 98% concentrate with a density of about 1.84 or 15.3 pounds (about 7.0 kilograms) per gallon (3.8 liters). Due to its density, a 10% by volume bath would be about 18% by mass. The dilution of the acid generates a great deal of heat. The acid is always added to the water and never the other way around, as the acid will cause the water to boil and spatter the acid. The acid used will normally range from 5 to 30% by weight at about 60 to 70° C. Tanks should be made of acid resistant stainless steel or polypropylene and use quartz or Teflon coated heating elements.

2. Muriatic (brick acid) or hydrochloric acid comes in a 28 to 32% solution with a density of about 1.2 or 10.0 pounds per gallon (about 4.54 kilograms). Solutions stronger than 50% by volume with mineral free water will generate strong fumes of hydrochloric acid which are quite irritating. For this reason, this acid is only used at an ambient temperature. At a 20% dilution by volume with mineral free water, it may be used at temperatures up to 140° F. (60° C.), but it is normally used at 30% to 50% by volume with mineral free water and at an ambient temperature. It reacts more rapidly than sulfuric acid and it is the acid of choice when you want to get a good etch on aluminum for adhesion. The first patent issued for getting Teflon to

stick to an aluminum surface was based upon the use of hydrochloric acid.[1] This type of deeply etched surface is a unique interaction with aluminum and the chloride ion. Hydrofluoric acid increases the rate of attack by the hydrochloric acid. Tanks may be polypropylene or hard rubber.

3. Phosphoric acid is sold commercially as a 75 to 85% solution by weight. 75% is the more common of the two. 75% has a density of 1.57 or 13.1 pounds per gallon. It is much less active then sulfuric or hydrochloric acid and is generally used at 15% to 35% at temperatures of 115° F. to 170° F. (46° C. to 77° C.) for light etching on aluminum. Phosphoric acid generates little heat when mixed with water and is used in stainless steel or polypropylene tanks. Adding about 1% ammonium bifluoride greatly improves the etch rate of aluminum when used in 15% to 35% phosphoric acid baths.

4. Nitric acid is generally sold as a 68 to 70% solution in water by weight with a density of about 1.42 or 11.8 pounds per gallon (1.42 kilograms per liter). It is strongly corrosive and a very strong oxidizer, particularly at high temperatures. At concentrations of 20% by weight, the acid will passivate aluminum and stainless steel and it should be noted that when 20% by volume of the 70% by mass acid is added to 80% by volume water, you will generate a 20% by mass solution of the pure acid. This acid will turn your skin a yellow-brown color on contact. It is the most expensive of the mineral acids and it is only used when other acids are not effective. Like hydrochloric acid, nitric acid will strongly fume at concentrations of 50% or above. The acid may be used in stainless steel tanks at a 20% or higher concentration by mass or in polypropylene tanks at any concentration. Nitric acid solutions of 10% to 20% are often used when mixed with 1 to 2% % ammonium bifluoride to deoxidize heavy metal alloyed aluminum alloys in aerospace applications. Concentrated commercial nitric acid (68 to 70%) mixed with 15 to 25% concentrated sulfuric acid (95 to 98%) and 3 to 5% ammonium bifluoride is often used on cast aluminum alloys with high silicon, iron, and copper content. It is the only way to effectively clean smut off many of these alloys and, in some cases, phosphoric acid (85%) may be included in the mix to give a clean white finish.

5. Hydrofluoric acid is the most corrosive and dangerous acid available, as it will dissolve almost anything except the noble metals such as platinum. It is used in concentrations of a few percent with nitric acid to remove heavy metal smut from high heavy metal content aluminum alloys. It comes in a

---

[1] Warmant, G. and Tartinville, J. 1954. Brit. Pat. 815,756

70% water solution, but because of its corrosive nature most people prefer ammonium bifluoride, which is also almost 70% fluoride.

6. A number of organic acids may also be used, such as citric, gluconic, and tartaric, as they are also good agents for the sequestration of elements, such as copper and iron, which are present in many aluminum alloys. These acids are often used with about 1 to 2% ammonium bifluoride to remove aluminum oxides.

7. Iron plus three sulfate or chloride is available and is a strong acid by itself; however, it tends to leave iron deposits on the aluminum articles being processed.

8. Chromic acid may be used but, due to the fact that it is a known cancer-causing agent, it now has little use in the aluminum finishing business. In addition to being able to remove metal oxides and smut, it will leave a thin protective film of chrome oxides.

A number of acid-based cleaners may be produced from the acids listed above by blending them with one or more amine-based soaps and/or any one of a number of acid stable surfactants. In addition, there are a number of expensive, but quite useful, fluorocarbon wetting agents. Phosphoric acid-based cleaners are favored for most of the commonly used aluminum alloys, such as the 6000 series. They are popular because phosphoric acid is quite safe. This substance is actually found naturally in a number of fruits and vegetables and it is added to many commercially available fruit juice products. Phosphoric acid will pacify aluminum and most of its alloys. In many areas of the country, there are restrictions on the discharge of phosphates because they promote the growth of various unwanted plants (weeds), but phosphates and any fluorides added to a given cleaner can be rendered quite insoluble with calcium carbonate or calcium hydroxide. For most lightly soiled or lightly oxidized aluminum alloys, phosphoric acid is blended with a small amount of fluoride and is an excellent cleaner and deoxidizer. In addition, the added fluorides will strip away any light films of elemental silicon or silicate residue. For these reasons, phosphoric acid-based cleaners are often used to clean aircraft, trucks, and so on. In all cases, the fluoride concentration must be kept rather low to prevent etching the aluminum, as well as for environmental reasons. In many cases, various hydroxyl organic acids, such as gluconic or hydroxyacetic, are added to phosphoric acid cleaners to assist in the removal of buffing compounds without harming bright or polished finishes.

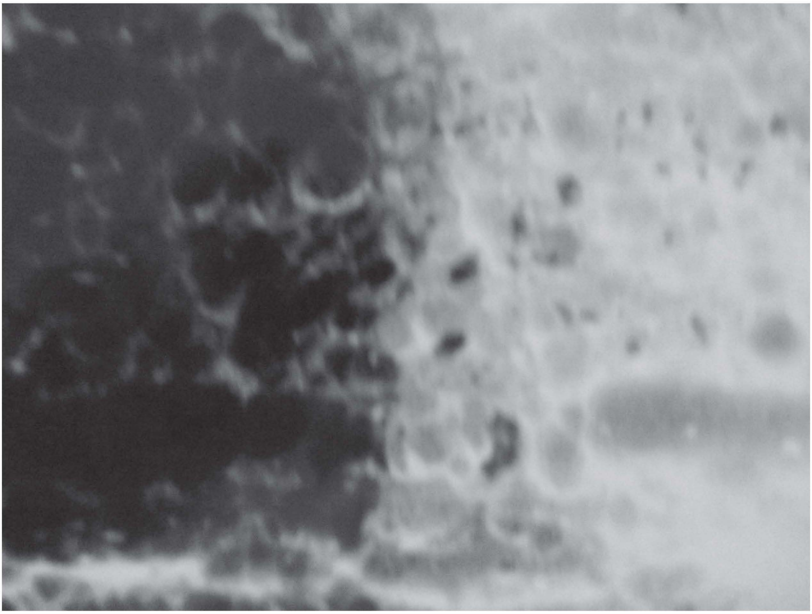


Figure 2.3 Aluminum surface cleaned in an iron containing deoxidizer, note the iron deposit.

If you are working with aerospace alloys that have up to 10% or more of alloyed heavy elements, such as copper, iron, or zinc, you will probably need to use 10% to 20% nitric acid with about 1% ammonium bifluoride to clean off the smut left on the alloys after alkaline cleaning. Using 20% or stronger nitric acid will passivate the alloy, thereby making it difficult to generate a conversion coating on the alloy. To get around this, quickly (just a few seconds) dip the alloy in a strong alkaline (pH 12 or higher) solution to get rid of the passivity in the alloys. This should be followed by a short rinse in mineral free water. If you are working with castings that may well have over 20% of alloyed elements, you will have to use concentrated nitric acid blended with about 15 to 20% concentrated sulfuric acid and about 5% ammonium bifluoride to get a clean and receptive surface. Needless to say, most shops will not want to work with this acid mixture due to its toxic nature but it is the best way to clean these castings and much safer than older methods that added chromic acid to the mixture. As in the case of the wrought alloys, the nitric acid will passivate the castings and you may need to get rid of this with a short (a few seconds) dip in a strong alkaline solution followed by a short rinse in mineral free water before conversion coating, as otherwise you will end up with some areas of the casting having little or no conversion coating and other areas with excessive amounts.

Alkaline Etching and Cleaning

The outer oxide film of aluminum and its alloys is much more easily removed under alkaline than under acid conditions. Additionally, the hydrogen released is quite useful at removing organic soils, apart from amine-based metal working fluids. If amine-based metal working fluids are present, use a phosphoric based cleaner to remove them before any alkaline cleaning or etching. Alkaline or acid cleaning should always come before any alkaline etching, as otherwise you will have uneven etching/or cleaning due to a lack of etching in soiled areas. Alkaline etched aluminum and its alloys will normally give you a frosted look because of its granular structure and alloys. In most cases, aluminum is alkaline etched before anodizing. It should also be noted that the addition of alkali nitrates (sodium or potassium) at about 1% greatly decreases the etch rate and improves the uniformity of the etch. In another direction, the addition of stannous (tin) ions will increase the rate of attack by the alkali, as will cobalt, but the rate of increased activity depends upon the alloy you are etching. The "5052" alloy will be attacked at an 86% faster rate with the addition of stannous ions,[1] while the addition of strontium, barium, and calcium will slow the rate of attack, according to Robert Elliott.[2]

In many facilities the etching is carried out with sodium hydroxide, but potassium hydroxide is less expensive and a stronger alkali. Eventually any aluminum etching tank will become saturated with aluminum hydroxide and it will start to fall out of the solution. The approach used in Asia, and probably the best approach, is to simply make dumps from the etch tanks on a regular basis to keep the aluminum hydroxide from falling out of the solution. Should the aluminum hydroxide fall out of the solution, it will create a difficult problem.

The type of alloy you use has a strong influence on the type of finish you end up with. Essentially pure aluminum has a fine-grained structure that is desirable for many applications. High heavy metal aerospace alloys are quite grainy. "6000" series silicon content wrought alloys always have a matte finish. The characteristic finish of each alloy is related to the amount of metal that has been removed. In most cases not more than 0.001 inch of

---

[1] Elliott, Jr. R.H. 1959. Pennsalt Chemicals Corp., US Pat. 2,918,357

[2] Elliott, Jr. R.H. 1959. Pennsalt Chemicals Corp., US Pat. 2,882,135

metal will be removed. "2000" and "7000" high heavy metal content have a deeper etch and grainier surface. Cuts and nicks will not go away and will only continue to get more rounded edges. Badly cut aluminum may require the removal of up to 0.003 inch of aluminum, but the cuts will persist. Both the temperature and the concentration of the alkali are quite linear curves. After about 17 to 26 ounces per gallon of aluminate (sodium or potassium) the viscosity of the bath causes a reduction in the etch rate and it becomes increasingly difficult to rinse the articles being processed. As mentioned earlier, you may dump out about half the bath and add fresh alkali, or try and slow the process by adding chelating agents. There are "EPA" regulations regarding dumping, but the materials in question are not that toxic and not a major problem in terms of disposal.

Alkaline Cleaning

As mentioned in the previous section, aluminum and its alloys are much more sensitive to alkaline conditions than to acid. As a result, alkaline cleaners have built in inhibitors to slow down an alkaline attack while maintaining a degree of alkalinity. In all types of light metal cleaners, it is essential that there is some degree of attack on the metal itself in order to be effective at removing unwanted metal oxides or attached soils. You will also always find a thin film of wax or oil on the degreased aluminum parts as the metal will have some degree of attachment for soils due to its thin film of metal oxides or electrostatic attachment. It has a "sea of electrons" that are unevenly distributed over the surface of the metal.

In most cases, alkalinity is 9.5 to 12.0 pH and buffered to maintain this. It needs to wet out any given aluminum surface and it requires good emulsifying agents for oils and waxes. It must be able to disperse any fine particles of dirt. It should be able to work in high mineral content water. In other words, it must have good chelating agents, but the best cleaning will come from mineral free water sources. It must also be an affordable cleaner. At the high pH end of aluminum cleaners, there are inhibitors added to the cleaner to mitigate the alkaline attack on the aluminum. Silicate is by far the most effective of the inhibitors but it is no longer used as this ability is high enough to actively prevent cleaning. As a consequence of chromates' toxicity, they are no longer used in most industrialized countries. Fluoride is also toxic, but not to the extent that it cannot be used in aluminum cleaners. It maintains a thin form of insoluble aluminum fluoride on the aluminum being cleaned and is quite effective at removing unwanted silica, as well as other unwanted elements and aluminum oxides. There should be minor gassing from the aluminum to indicate that cleaning is taking place. This initial gassing slows during the cleaning process but never quite stops. Nitrates are quite effective at doing this and next are phosphates. Excessive gassing in parts of the meta is an indication of corrosion or past etching. This may require acid etching to get a more even gassing in the alkaline cleaning tank. Most commercial alkaline cleaners depend upon alkaline phosphates or carbonates.

One of the most important things to keep in mind with alkaline cleaners is to not add an excessive amount of cleaner to the bath. If you have added the recommended amount of cleaner and you are still not getting a "water break free" surface, do not simply add more cleaner. This is because you will eventually get a surface that will always be "water break free", as you will no longer be able to rinse the soap off the article. All commercial cleaners will have data sheets complete with procedures to check on the active cleaner content of your bath. A useful, but crude, test for excessive cleaner is to find the pH of the rinse tank which should be no more than 8.5.

The "dragout" of cleaner can be quite expensive, depending upon the cleaner used and the parts being cleaned. As a general rule, vertical parts with no cup shaped areas will pull out about 0.6 to 1.5 gallons of cleaner per 1000 square feet cleaned. Horizontal parts will pull out about 1.4 to 8.0 gallons per 1000 square feet and "cup like" shaped parts may pull out as much as 10 to 20 gallons per 1000 square feet. Overflow rinse tanks should be designed for 5 to 8% of their volume per minute. Another method to save money on cleaner is to spray a fine mist of clean water right over the tank to wash a significant amount of the soap back into it. If the volume of the parts are quite high, reverse osmosis will also save you a lot of money. Keep in mind that the higher the quality of the water you are using, the greater the cost and the better the cleaning. Reverse osmosis will, as a general guide, give you water of about 15 PPM to 10 PPM which should be acceptable for most metal cleaning processes.

Magnesium

Going back to the 19th century, strong alkaline solutions were always used to clean and passivate magnesium surfaces; this is because alkaline solutions will build up a thin protective film of magnesium oxides and carbonates on the metal. Cleaning solutions for magnesium are almost all alkaline (the pH should always be 11 or higher) at the boiling point and should not contain much more than some simple wetting agents, as otherwise you risk having the soaps attach to the surface of the magnesium because it is a very chemically reactive metal.

The best method to clean magnesium and/or its alloys is to make the metal the cathode in a 5% potassium hydroxide solution for about 15 to 30 seconds followed by rinsing in mineral free water. Potassium hydroxide is used as it is a stronger alkali then sodium hydroxide; it is also less expensive and may leave insoluble residue on some magnesium alloys. The release of hydrogen in the magnesium cathode is quite effective at removing soils from the metal and most alloyed elements. Depending on the alloy you are working with, you may have to follow up the alkaline cleaning with a dip in a mild acid solution (3 pH approx.), such as nitric acid at a low concentration for a few seconds. This must be followed by rinsing in mineral free water. If you leave the magnesium too long in the acid, you will have to go back to the 5% potassium hydroxide solution and repeat the cleaning procedure.

Titanium

Titanium does not differ much from magnesium with regard to cleaning but, unlike magnesium, titanium and its alloys are rather inert to strong acids as its outer layer of oxides are very difficult to remove and, when removed, will quickly reform. Any smut that may develop during the alkaline cleaning may be removed with a quick dip in a strong (20% or above) nitric acid solution, containing about 1% ammonium bifluoride.

Beryllium

The use of beryllium is generally restricted to aerospace applications and it is a very toxic metal to work with. Therefore, use protective clothing when working with it. Like titanium, beryllium has a very strongly adhering film of attached oxides that will require the use of strong nitric acid (20% or higher) and 5% ammonium bifluoride. Any attached loose dirt, metal working fluids, lubricants, and so on may be removed by making the metal the cathode in an electrochemical cell consisting of 5% potassium hydroxide for about 30 seconds.

Electrocleaning light and heavy metals

Electrocleaning applies to all of the metals discussed and it is used when the metal needs to be as clean as possible. This should occur all the way down to the bare metal, if possible. In most, if not all, of other types of cleaning, there is always a thin film of soil of one kind or another on the metal, but it is not an issue in that the conversion coating process will ingest the soil. It will, therefore, become part of the conversion coating, which means there will not be an issue. In the case of metal plating and other types of conversion coating, it may well be an issue.

The article to be cleaned becomes either the anode (positive) or the cathode (negative) in an electrochemical cell, which consists of an acid base or neutral solution. This allows the cell to conduct and release oxygen or hydrogen. The generation of large amounts of hydrogen or oxygen will "scrub" the surface of the metal. Oxygen may be needed to oxidize and lift off a particular type of soil, or you may want the reducing effect of hydrogen; this will depend on the metal you are working with. Electrocleaning is generally designed to be used right after an acid or alkaline cleaning process and a series or rinses to remove as much residue as possible. The electrochemical cell needs to be as free as possible of any stray metals or oxidants that could have an adverse effect on the article to be cleaned. In some cases, a facility will have two electrochemical cleaning tanks as conventional alkaline or acid cleaning is simply not good enough; this is also necessary to prevent any carry over from the previous acid or alkaline cleaning procedures. In many cases, a non-ionic wetting or cleaning agent will be added to the electrocleaning tanks to keep soils from redepositing themselves on the article being cleaned. The addition of cleaners means a foam blanket will form that will then allow the electrolyte to flow back into the tank. It is important to prevent it from entering the atmosphere as it can be caustic. This may be an issue in that both hydrogen and oxygen are released and a stray spark will cause an explosion but, in most cases, such explosions are rather small. Another issue is that the foam may dry on the articles when removing them. One way to get around this is to spray a light mist of water over the articles as they are removed. Metals that are easily oxidized, such as aluminum, stainless steel, and nickel, are cleaned cathodically. Brass is cleaned cathodically to keep the zinc from being dissolved. If silicates have been used as an inhibitor, then the metal must be cleaned anodically as cleaning cathodically will only make it more difficult to remove.

Iron and its alloys may be cleaned anodically or cathodically but it will brown under anodic conditions at high current densities, which is another way of saying it will oxidize. An inhibitor will restrict the cleaning process. Stainless steel may also be cleaned anodically, but it will also tend to oxidize. Cathodic cleaning is generally used on nickel. Nickel plating is cathodically cleaned to prepare it for chrome plating. Zinc die castings or copper parts may be cleaned cathodically or anodically, but anodic cleaning is preferred to avoid unwanted oxide films. Lead is generally cleaned cathodically to avoid anodic staining and etching. Brass is generally cleaned cathodically with a short reverse current stage to remove smut.

The current density affects the finish and the uniformity of the current distribution. Most facilities are more concerned with the voltage than the amperage and most facilities operate at about 3 to 6 volts. Using a high current to darken or tarnish the article in electrocleaning is acceptable if the oxide coating is uniform and easily removed with an acid dip.

Removing smut from steel is difficult and electrocleaning is probably the best procedure to tackle this. Most smut consists of iron carbide as a result of etching the steel. Another source of smut is rolling or drawing lubricants that have decomposed from heat treatments and formed elemental carbon. Removing this smut is important as much of this steel will end up being electroplated and you cannot electroplate smut. The best way to blast off the smut is to generate large amounts of hydrogen. The baths are generally operated at about 175 to 210° F. This improves the mobility of the ions to strip the smut off. The composition of electrochemical baths when stripping smut is generally potassium or sodium hydroxide covered with a good foam blanket to keep the electrolyte in the bath; it is important that the soaps or surfactants used are stable under these conditions. Fluorocarbon surfactants are often used under these situations despite the expense involved. In many cases, the polarity will be reversed. A typical cycle under these conditions is 20 seconds anodic and 10 seconds cathodic. A longer anodic cycle is used as a means of oxidizing any free iron that may be generated, so that it is easily removed. Even if you have not added soap to your cleaning bath, there may well be buffing compounds and lubricants on the articles, which tend to be attracted to the electrodes. For this reason, the articles should be given a good soak cleaning before going into the bath.

After electrocleaning, the steel article may be given a cyanide plating bath strike deposit made up of zinc, nickel, silver, or copper to maintain an oxide free surface and to have a well bonded metal on the surface of the steel. The strike also serves as a cleaner and conditioning step as cyanide is quite alkaline. The cyanide removes any remaining oxides, but environmental issues have restricted its use.

Ultrasonic Etching Steel

A very high frequency sound, beyond human hearing, is able to vibrate a sheet of steel in a water-based solution so that bubbles collapse on the surface of the steel, which then generate very high instantaneous hydrostatic pressures that rip off particles of soil. Acid etching steel using sulfuric acid will give the same etching action in about one tenth of the time normally required with the added benefit of removing the soil. In addition, there is less hydrogen embrittlement because there is less exposure to hydrogen. In most cases, the smut can be wiped off the steel, although this is dependent on the article's surface condition. A focused beam of ultrasonic sound can be used to reduce the etching rate by about 1 second when moving at 500 feet per minute, thereby also creating a reduction in the length of the tank by about 11 feet.

Soak Cleaning

In the vast majority of metal cleaning, an alkaline solution is used in conjunction with a soak tank. This is particularly true with heavy metals and cleaning continues to be the most important aspect of any conversion coating process. The tanks will generally have a slope as, in many cases, the metals being cleaned will have heavy oxide soils that may be easily isolated and removed from the tank on the sloped side with a false bottom insert. Immersion cleaning will generally give the best results as the article being cleaned will be hit from all sides by the cleaning solution and it is also usually the least expensive method. The tank should have an adequate distance between the walls and the work, so that the work will not hit the walls of the tank or the heating coils. The workload should not go beyond 25% from the bottom of the tank to minimize stirring up sludge and debris. If you do not want to have a sloped bottom, you may want to pump the spent cleaner into another tank with a conical bottom where the sludge can settle and be discarded. The tank should also have a skim trough to remove floating soil and debris. This can be completed by overflowing the cleaning tank by adding additional water. This should occur at least once a day or more often, depending on the soil on the articles being cleaned. The best time to do this is after the cleaning tank has been dormant for about 8 hours. There are good and bad features in this heating process. It can be heated using steam coils, direct fired boilers, plate coils, or immersion electric heaters. Due to the huge heat capacity of water, steam coils are probably the most efficient way to transfer heat the cleaning solution. These should be stainless steel at about 100 p.s.i. to avoid possible corrosion issues. Plate coils have a very concentrated heat sources and should also be made of stainless steel. If 100 p.s.i. steam (about 290° F.) causes difficulties, use a reducer to bring the temperature and steam pressure down to about 25 p.s.i. Another source of heat is direct firing through an inner tube where steam is not available. To avoid any corrosion problems, the heating tube should be made of "Monel" or "Inconel". Electric immersion heaters tend to be somewhat expensive, but may also be used as a source of heat for the cleaning bath. They do allow for more precise control of temperature once the bath has been heated to the necessary temperature. Another way to conserve heat is to have a single wall between the soak and rinse tanks. If the other tanks are not rinse tanks, you run the risk of the soak tank contaminating the other tanks and causing problems with the cleaning process. Soak tanks will, in many cases, have ventilation ducts or fans to remove steam and fumes, which may condense the water and cause corrosion problems when the tanks are not in use. The soak tanks will need agitation but, in most cases, just the process of placing the parts in the tank and then removing them should be sufficient. If not, pumping the cleaning solutions over the submerged articles is only useful with a high capacity pumping system. This method is often used with cleaning bundles of piping to clean the interior of the pipes. Agitators may be used in a soak tank, particularly with the use of a solvent based cleaner. Circulation with a mechanical stirrer does not work well. Air agitation does not work well at all and only creates a lot of foam and cools the cleaning solution. Air agitation is only effective in rinsing operations. In addition, air agitation will lower the pH of your alkaline cleaning solution as the carbon dioxide in the air will decrease the alkalinity of the bath. Alkaline soak cleaners are generally used in the range of about 165 to 200° F. At high temperatures, more effective cleaning is needed to turn the soils into a liquid. Very little cleaning is accomplished at an ambient temperature unless the cleaner contains a high content of solvents or surfactants to liquefy the soils. Cleaning times will vary according to the type of soils being removed, but on average you will need at least 3 minutes, but not more than half an hour, on this task. The average concentration level for alkaline soak cleaners will range from 3 to 11 ounces per gallon, with 5 to 8 ounces being the average. As a general rule, using more than 10 ounces per gallon will have little or no effect on cleaning and will make it very difficult to rinse the cleaner off. For paints or polymerized oils, it is important to use as high a pH as possible (12–13). Highly alkaline cleaners will have no adverse effect on magnesium, steel, or nickel alloys and magnesium should have a pH of 11 or above. High pH cleaners may tarnish copper and remove zinc from brass. Strongly alkaline cleaners will tarnish zinc, lead, aluminum, and tin.

Spray Cleaning

The advantage gained by using a spray system is its impingement on the soiled metal surface being cleaned. For this reason, the cleaners may be much milder than those used in soak systems. Another advantage to the spray system is the decrease in cleaning time. While a soak cleaning system may take from 4 to 15 minutes, a spray system will only take about 1 to 4 minutes to achieve the same degree of cleaning. This increase in cleaning time makes the process well adapted for high capacity cleaning processes, but the spray system is more expensive to install and operate. The spray system requires low foaming cleaners and control over the foam that is produced. The surfactants that generate the most foam are the most effective at removing soil. As a result, less efficient cleaners end up being used with any spray system and spray cleaning solutions generally end up only using about 1/4 to 1.0 ounces per gallon.

Alkaline Spray Cleaning

High temperatures are both necessary and difficult to maintain in any alkaline spray cleaning process. Normal operating temperatures are about 140 to 180° F. Lower temperatures are used when "perfect" cleaning is not desired and, in many cases, this is done to stop steel articles from rusting by leaving a thin film of oil on the parts. The proper spray pressures and volumes are important with regard to foaming and cleaning. Normal pressures range from 8 to 35 pounds approximately per square inch, with 15 to 21 being the most commonly used pressures. Pressures above 25 cause excessive foaming and tend to throw the work off their hooks or racks. As a result, many facilities will use pressures as low of 3 to 10 p.s.i.; this floods the articles with a large volume of cleaning solution which, in many cases, is effective on loosely adhering soils, such as light oils.

Spray Equipment

Spray equipment needs to be designed so that the risers and pipes are located to allow for maximum impingement. The size of the spray chamber is dictated by the speed at which the articles being cleaned move and the production load. Quite often the area between the various cleaning and rinsing stages or cleaning and conversion coating sections is too small. The area between the processing stages must be long enough to allow for drainage and to prevent overspray, which would contaminate the various stages. Depending upon the shape of the articles being cleaned, you could have the cleaner or conversion coating completed at the next stage instead. Loose neoprene or rubber sheets are often used as a curtain to keep this from taking place and the cleaner or rinse should flow back to avoid contamination. Depending on the length of the area between the cleaning stages, you may want to use a fine mist of clean water to avoid cleaning residue drying on the parts. Solid cone whirl jets spray heads will give the best coverage and impingement pressure. "V-jets" or holes cut in the pipe are not as effective due to inadequate levels of control and coverage. Alkaline cleaners are generally used with "V-slots" or "V-jets" as they require less maintenance to manage clogging. As a general rule, the spray heads should be checked for embedded particles once a day.

Alkaline Oxide Removal

As a general rule, most metal oxides are removed by acids. However, this process will not remove embedded organic soils and it will also remove a significant amount of metal along with the oxides. A number of alkaline baths will remove rust and organic soils without attacking the metal being cleaned or causing hydrogen embrittlement. These are concentrated (50 to 80 %) caustic soda or potassium hydroxide solutions at about 200° F. but may also be used at lower temperatures. In addition, they may also contain various oxidizers, such as potassium nitrate, chelating agents, and surfactants, for their cleaning actions. The removal of elemental iron is quite small with these products. It is recommended that stainless steel be used to contain the derusting baths as they may attack iron. Baths of this type were mentioned earlier in the section on iron oxides. The strong alkali will actually react with the iron to initially form iron hydroxides which may then go on to form the black magnetic oxide of iron. In this instance, the iron is already covered with the red iron plus three oxides that are dislodged from the surface of the iron, but the iron hydroxides are "tied up" with chelating agents. Agitation is an important factor in their use, as it breaks the grip of any iron oxides in the iron or iron alloy. The rusted iron or steel parts are kept in the bath for about 5 to 15 minutes, removed, and then sprayed down with water. The process is repeated until the rust is removed. The heavier and the more weathered the rust, the longer this procedure will take. There is no easy way to decide when to add more of the non-alkaline ingredients other than to have standard rusted panels to use as a check on how well the derust solutions are working. The extent of any adjustments to the composition of the deruster will have to be worked out by your own experience.

Electrolytic Alkaline Derusting

The above alkaline derusting is improved by the application of an electric current that will then generate oxygen and/or hydrogen that greatly increases the ability to "chip away" attached metal oxides and other soils such as old paint. In many cases, the article to be cleaned is alternatively switched from cathode (hydrogen release) to anode (oxygen release) in 10 to 15 second cycles to improve the cleaning. Current densities must be kept high, which also increases the overall cost of the operation, but very little, if any, metal is lost in the operation. Current densities are generally maintained in the range of 120 to 160 amps per square foot. The process may be shortened by the addition of chloride ions, but this runs the risk of anodic pitting, particularly with nickel based stainless steels. Another effect is the plating out of iron and other alloyed elements, as any added chelating agents will be oxidized by the process. In point of fact, iron will build up as iron hydroxides or, in some cases, iron plus six iron salts will have to be removed by plating the iron out on a discardable electrode.

Acid Oxide Removal

The "mill scale" is the oxide film left on mild steel after hot rolling or forming. The oxide layers consist of ferrous oxides (iron plus two), ferric oxides (iron plus three), and magnetic iron oxide that consists of iron plus two and iron plus three oxides. Sulfuric acid is almost always used to strip the oxides as it is the least expensive mineral acid, which is still strong enough to remove the oxides. Ferrous oxides are easily dissolved by the acid and are very loosely attached to the steel. The most strongly attached is magnetic iron oxide and this can only be removed once the hydrogen, which is generated by reacting with the iron, lifts off the oxide. In order to do this, the steel is deformed to generate cracks in the magnetic oxide film. The rate of iron oxide removal will increase until you get above 25% sulfuric acid, at which point the sulfuric acid's oxidation (sulfuric acid is a strong oxidant) begins to exceeds the rate at which the iron is able to reduce the hydrogen ions into free hydrogen gas. Concentrated sulfuric acid may be stored in steel drums but, in general, this is not done, as sulfuric acid strongly attracts water and then becomes diluted. Impingement of the acid against the steel with a high pressure spray is quite effective as it generates cracks in the magnetic oxide film. Once the concentration of dissolved iron reaches 5%, the rate of scale removal is cut in half for a 10% sulfuric acid solution. In industrial iron oxide removal, the ideal conditions are sulfuric acid concentration of between 4.5% to 15.5% by volume, 135 to 175° F., and 6 to 50 minutes in a soak tank. In actual production, the sulfuric acid concentration is generally maintained at about 10% by volume. In waste disposal, the acid needs to be neutralized. Hydrochloric acid is more expensive and there are fumes to contend with but it may be used at an ambient temperature and does not leave insoluble metal salts or smut. It is generally used at 12 to 25 % by volume for 2 to 6 minutes at room temperature. Another advantage to hydrochloric acid is that it may be almost completely used up before it needs to be disposed. This is because hydrochloric acid tends to pit the steel and so it is often used with an inhibitor that slows down the rate of attack in the steel. Phosphoric acid is even more expensive than hydrochloric acid and will not pit or leave smut on the metal. It will actually leave a passive film of iron phosphates. This means that it may be used to remove hard water scale, milkstone, beerstone, and so on from stainless steel in food processing industries.

Acid Activation Oxide Removal

Quite often a light oxide film prevents the deposition of another metal. For example, the tin deposition on steel, zinc deposition on steel, or electroplating nickel. This involves the use of any one of a number of mineral acids at low concentrations or, in some cases, a mild organic acid such as citric acid. It is also sometimes difficult to remove oxides from various stainless steels as they may be susceptible to hydrogen embrittlement and a number of acid systems have been proposed. Austenitic stainless steels may have their oxides removed with a ferric sulfate, hydrofluoric acid mixture. It is also used on straight chromium steels that are first processed in an 8 to 15% volume sulfuric acid solution at about 160° F. The composition of the ferric sulfate-based acid is about 7% ferric sulfate and 2% hydrofluoric acid (100%) at about 165° F. The same concentration level of hydrochloric or sulfuric acid has been used. All of these iron-based acid treatments are followed by a 10 % nitric acid, 1% hydrofluoric acid dip at 130° F.

Acid Aluminum Oxide Removal

As mentioned earlier, phosphoric acid-based cleaners are very effective at removing the outer layer of oxide and will not etch the surface of aluminum, but fluoride is necessary to remove any silicon or silicate residue from a cleaner or ground water sources that are high in silica content. Hydrochloric acid will effectively remove the oxide layer, but will pit the aluminum and, in point of fact, hydrochloric acid is used to "key" the surface to attach the "Teflon" in cooking pans. The removal of oxides before "spot welding" aluminum is a major concern and, for some time, this was accomplished by the use of chromic acid-based systems, but it is now not used as it is a known cancer causing agent. On the acid side, the only good replacement for chromates are high fluoride content phosphoric acid baths, but the best overall oxide removal procedure appears to be using an alkaline based system.[1]

Acid Magnesium Oxide Removal

Magnesium quickly forms a loosely bonded oxide film when exposed to the atmosphere, which makes it very difficult to weld or plate. Unfortunately, the acid removal of magnesium oxides has been dominated by the use of chromic acid formulations since 1920 and, in point of fact, they do not work that well. Chromate-based formulations do not establish a firm grip on the surface of magnesium. The formation of an inorganic polymer network will not develop under the alkaline conditions that constantly exist on the surface of magnesium and magnesium chromate is soluble in water. The best agent for the removal of magnesium oxides is hydrofluoric acid, which will form a very insoluble film of magnesium fluoride.

Rinsing and Drying

After removing as much soil as you want from a given piece of work, you have to rinse the cleaners off. More effective rinsing will improve your conversion coating. The first issue is to consider how clean a rinse you need. Some of the cleaners may well be dragged into the rinse tank water and that may be acceptable. Assuming you are using a rinse tank and are working with well drained vertical parts you may expect a "dragout" of about 0.4 to 0.5 gallons of cleaner for every 1000 square feet of processed metal. For poorly drained parts, you can expect about 2.0 to 2.2 gallons. For horizontal parts that are well drained, you can expect about 0.8 to 1.0 gallons. For horizontal parts poorly drained expect about 10.0 to 15.0 gallons. Cup shapes are difficult to determine without knowing their size, but range from about 10 gallons to 20 or more. The methods of racking and/or stacking will make a difference. Drainage should be tilted into the cleaning tank, but too long a period will allow for the cleaner to dry on the parts and may cause

---

[1] Ihsan K. Al Naimi, Moneer H. Al Saadi, Kasim M. Daws & Niels Bay. 2015. Influence of surface pretreatment in resistance spot welding of aluminum AA1050, Production & Manufacturing Research, 3:1, 185–200, DOI: 10.1080/21693277.2015.1030795

unwanted oxidation. A good option is to use a fine misting spray over the parts to wash the cleaner back into the tank. Another option is to have a double rinse system with one warm water rinse and one cold water rinse. Too hot an initial rinse may result in rapid drying of the parts as they come out of the first rinse, which could leave residue that will not come off in the second rinse. Rinse tanks with water in the range of 115 to 140° F. appear to give the best overall results.

The rinse water flow is important, as you do not want any areas in the rinse tank that have higher amounts of cleaner. As a general rule, fresh water should flow in from the bottom of the tank and out at the top. In some cases, you may want to have one or more baffles to spread the fresh water through the tank. There have been a number of studies on the optimum flow rate of fresh water through the rinse but they cannot possibly take into consideration all the possible variations with regard to the concentration of the cleaner, type of cleaner, operating temperature variations, and so on. The most important conclusion from these studies was that having two rinse tanks makes a big difference to the contaminant concentration in the final rinse tank, as might be expected, but having three rinse tanks did not make that much of a difference. The rinse tanks should be as small as necessary for the work load and the water flow maintained as high as needed to get the contaminant to your desired level. The water should be agitated as much as possible. If both rinse tanks are at the same temperature, the second tank should be about 2 inches higher than the first tank. This will allow the countercurrent flow of the water from the second to the first tank; this process will save water.

Spray Rinsing

Most of the issues discussed regarding the use of tank rinsing will also apply to spray rinsing because it is far too expensive to use only fresh water. Spray rinsing comes from recirculated baths and, as such, the number of tanks and water flow are just as significant. Much of what was discussed in the section on spray cleaning also applies to spray rinsing: the proper positioning of the drainage troughs, reducing overspray with the use of curtains, and so on.

Drying

The rinse water may well contain dissolved salts and, as a result, as much water as possible should be allowed to drip or be blown off the parts. Rapid drying is generally not a good thing, because water is a good oxidizer, excessive heat may cause oxidation stains.

CHAPTER 3

LIGHT METAL CONVERSION COATING SYSTEMS

Light Metal Chromium Based Conversion Coatings

The most stable oxidation state for chromium salts is plus six. You can try and stabilize chromium in a lower oxidation state, but it will eventually convert itself to the plus 6 oxidation state. In the plus 6 state, chromium is a known to be carcinogenic agent. This presents a problem in the metal finishing industry because, otherwise, it is an excellent conversion agent for both heavy and light metals that resist corrosion.

In the plus 6 oxidation state, chromium will generate chromic acid when added to water. The acid will attach itself to the metal or metal oxide to be conversion coated and will also attract water to form an inorganic polymer consisting of chromium plus 6 and water. The polymer will also contain lower oxidation state chromium salts. Due to the fact that the metal is a good reducing agent, it will also create salts. With both light and heavy metals, the polymer formation takes about 6 to 8 hours to complete, at which point water will bead on the conversion coated metal making it difficult to accept paint. As such it is recommended that any painting be completed in the first hour after the application of the conversion coating solution. Heating the conversion coating above 80 to 90° C. is not recommended as the polymer will decompose. Chromate based conversion coating systems are excellent for corrosion resistance, but have poor paint adhesion.

The wide spread use of chromate based conversion coating began in the 1920s when the U.S. and British navy started using chromate based conversion coatings on the aluminum sections of their ships. Specifications around the use of chromates on aluminum soon followed and then spread to other light and heavy metal systems. In the 1990s the U.S. Navy developed and obtained patents[1] on trivalent chromium systems that initially required the use of strong oxidants, such as hydrogen peroxide or permanganate,

---

[1] U.S. patent: 5304257

which would immediately convert any trivalent chromium to hexavalent chromium. A series of similar trivalent chromium systems followed. Prior to the U.S. patent filed by the U.S. Navy, there were other trivalent systems, but all of them employed some kind of strong oxidant[1] to generate plus 6 chromium. The first trivalent system that claimed to be completely trivalent (with no strong oxidant) was U.S. patent 6,287,704, but independent testing of these and other trivalent systems continues to show that, once the processed parts are in use and exposed to oxidative conditions, chromate is found on the conversion processed parts.[2]

Chromating Magnesium and its Alloys

Magnesium has an oxidation reduction potential of about + 2.34 V. relative to a standard hydrogen electrode, which means it is very easily oxidized and that the oxides and/or hydroxides found on the surface are quite alkaline. This means that it is very difficult to paint or coat it with anything, including conversion coatings designed to improve adhesion or corrosion resistance.

Magnesium chromate salt is soluble in water and will wash off as fast as it forms. One way to get around this is to add fluoride to your chromate conversion coating bath as magnesium fluoride is quite insoluble. This will work to a certain extent, but chromating on magnesium has not been very successful. A standard chromating bath for magnesium will not last more than half an hour in a neutral pH salt fog bath at 90° F. (about 32° C.): see ASTM specification B117. Magnesium phosphate is also somewhat insoluble, but soaking the magnesium in a water solution of 150 grams per liter phosphoric acid and 20 grams per liter potassium fluoride can be used to polish and harden the surface of both magnesium and its alloys. Chromating baths are generated by dissolving about 250 grams of chromium trioxide in a liter of mineral free water with about 5.0 grams per liter hydrofluoric acid to generate insoluble magnesium fluoride to trap and hold the chromate on the surface of the magnesium. Other additives have been tried with little success.

---

[1] U.S. patent 3,171,765

[2] F. Altmayer. 2004. "Testing Finished Parts for Hex Chrome", Plating and Surface Finishing, 91 (12), 20.

Chromating Aluminum and its Alloys

The oxidation reduction potential of aluminum is only about 1.67 V. relative to a standard hydrogen electrode, but it is still a very good reducing agent. Unlike the soft easy to remove powdery oxide on magnesium, aluminum has a more tightly held thin oxide coating that assists in retarding further oxidation to some extent. Given the huge volume of aluminum that is processed every year, literally hundreds of patents have been granted for conversion coatings on aluminum, but only a few have had significant amount of success. If their cancer-causing activity had not been discovered, they would still be the most widely used conversion coating system.

In the 1920s the initial processes for generating aluminum conversion coatings centered around alkaline solutions to generate aluminum oxides and hydroxides that would then react with added chromates.[1] The process were long and involved and did not have a lot of success. The first really successful commercial conversion coating processes were the chrome phosphate systems, which could be operated at room temperatures and provided for good paint adhesion, and the chrome fluoride process, which gave excellent corrosion resistance and could be operated at low temperatures. Both processes were first used in the late 1940s and early 1950s when aluminum production greatly increased.

Chrome phosphate processing solutions range in composition from 20 to 100 grams per liter phosphate, 2.0 to 6.0 grams per liter fluoride, and about 6.0 to 20 grams per liter chromium trioxide depending on the type of finish. The aluminum alloys with a high silicon content will need a higher fluoride content and the pH of the solutions should range from about 1.7 to 1.9. The coatings have a blue green color, which comes from the generation of chrome plus 3 oxides. They are designed to have good paint adhesion characteristics but the hexavalent chromium compounds are only good for corrosion resistance. The coatings still have a significant amount of hexavalent chromium compounds and so will have a certain amount of corrosion resistance. In "powder coating" applications, the relatively high temperatures (80° C approx.) used will, in most cases, destroy the water-based gel formed by the hexavalent chromium.

Chrome fluoride baths are more difficult to control and should remain at a pH range of about 1.5 to 1.9. The baths are generally operated at about 32° C. and the coatings range from colorless, when processed for about 30 to 40

---

[1] Bauer, O. and Vogel, O. 1923. German Patent 423,758

seconds to create paint adhesion and acceptable electrical conductivity, to a dark yellow when processed for about 2 minutes. The colorless coatings will have about 30 milligram per square foot of coating, while the dark yellow processed parts will have about 90 milligrams of coating per square foot. The baths will generally have a composition of about 4.0 grams per liter of chromic acid, about 3.0 grams of sodium dichromate, and about 0.8 grams per liter of sodium fluoride, but compositions will vary depending upon the manufacturer of the product and other materials, such as ferrocyanide, may be added to generate a more even coating and improve its corrosion resistance.

Aerospace alloys that contain relative high amounts of copper, iron, or zinc are difficult to coat in a uniform manner as the alloys are rather heterogeneous. This results in non-uniformity in chemical reactivity on the surface of the alloy. In order to correct this, dip the parts in a strong alkali solution (13 pH or higher) for a few seconds in order to get a uniformly activated surface. Then quickly rinse and go directly into the treatment bath. The corrosion protective value of chrome fluoride coatings is twice as strong as that found in chrome phosphate baths.

Chromating Titanium and its Alloys

The oxidation reduction potential of titanium relative to a standard hydrogen electrode is about the same as aluminum (about -1.6 V) and, like aluminum, it has a very tightly attached film of metal oxides that are difficult to remove and quickly return once the metal is exposed to the atmosphere. Titanium is quite resistant to corrosion so that most applications relate to paint adhesion issues. It is relatively easy to anodize titanium in order to obtain good paint adhesion. The only chromate-based conversion coating I am aware of consists of about 30.0 grams per liter of sodium chromate and about 20 grams of sodium fluoride per liter adjusted to a pH of 9.5 and used at an ambient temperature for about 10 minutes.

Chromating Beryllium and its Alloys

The oxidation reduction potential of beryllium relative to a standard electrode is about + 1.99, but it is relative inert and unreactive as its outer electrons are held rather strongly. The only published chromate conversion coating is found in U.S. patent: US3485682A, which belongs to the U.S. Army. It was issued in 1966 and consists of a bath containing about 200 grams per liter chromic acid and about 7.0 grams per liter fluoride as hydrofluoric acid. It allows the beryllium to withstand temperatures up to 900° F.

Light Metal Phosphate Based Conversion Coatings

Phosphate based conversion coating systems go back thousands of years. They are almost always used on heavy metals, such as iron and its alloys. Their primary function is increasing adhesion and they do little to improve the corrosion resistance of heavy or light metal elements. Light metals are not generally given a phosphate-based conversion coating as phosphoric acid does not form a good conversion coating by itself. In the section on chromate-based conversion coatings, phosphoric acid was an additive to a chromate-based conversion coating. In the section on anodizing, we will discuss phosphoric acid anodizing, but this is an anodizing process that uses phosphoric acid. Purely phosphoric acid-based conversion coatings are found in the heavy metal section of the book. The use of iron, zinc, and manganese acid phosphates on aluminum have not been very successful, as they leave deposits

on heavy metals which then gives rise to galvanic corrosion. In addition, heavy metal acid phosphates, other than chromate, pit the aluminum and generate more corrosion.

Beryllium

There are essentially no commercial applications for beryllium and the only industrial applications for titanium relate to medical applications[1] on a rather small scale.

Magnesium

As might be expected, magnesium will not form a good phosphate conversion in terms of paint adhesion or corrosion resistance. The only success has been with an acid manganese phosphate-based system containing a very high fluoride content in order to generate a large amount of insoluble magnesium fluoride. This consists of manganese dihydrogen

---

[1] Acta Bioeng Biomech. 2017; 19(2):65–72

phosphate at 80 grams per liter, manganese silicofluoride at 500 grams per liter, and potassium fluoride at 40 grams per liter.[1]

Aluminum

Phosphating aluminum began over 100 years ago as a way to obtain good paint adhesion. Initially, it only required a dilute phosphoric acid solution and prior cleaning of the aluminum in an alkaline solution, as alkalinity greatly activates oxidation. When using this process, you will get a thin aluminum phosphate coating that allows for paint adhesion. To improve the adhesion characteristics of the phosphated surface and to get a thicker and more corrosion resistant surface, which is not as corrosion resistant as a chrome phosphate, a mixture of various fluorides and heavy metals, such as iron, zinc, and manganese, and various oxidizers were added to the phosphoric acid. These solutions could then also be used on mixed metal surfaces containing aluminum, zinc, iron, or steel but their primary function was just to phosphate iron, steel, and zinc or zinc coated surfaces. A typical processing solution would be:

Manganese dihydrogen phosphate 342 grams per gallon
Manganese silicofluoride 1710 grams per gallon
Potassium fluoride 152 grams per gallon

In addition, the solutions could be mixed with a clay to which starch may have been added. The mixtures were allowed to dry on the article being processed for about 7 to 12 minutes and then the clay and starch were washed off leaving behind a coating with about:

Manganese: 30–32%
Phosphate: 36–38%
Fluoride: 4–6%
Aluminum: 0.8–0.12%

In some cases, cadmium was used in place of manganese, but if this is used in too large a quantity, it will plate out on the aluminum. In addition, cadmium is now considered to be a toxic material.

The 1940s[2] saw a series of various oxidizers added to the solutions to decrease the immersion time and to generate a finer crystalline structure,

---

[1] Thompson, J.S. 1943. U.S. patent 2,234,206 and 2,312,855; and patent 1,007,069
[2] Darsey, V.M. and Cavanagh, W.R. 1946. Electrochem. Soc. Preprint 91–1

which tended to give better paint adhesion. In addition, more fluoride was added to the baths. At the time, the most commonly used oxidizer was sodium nitrate, which was inexpensive compared to others, such as iodates, bromates, and peroxides. The immersion times were now reduced to about 2 to 4 minutes at about 60° C. An example of the solutions being used at this time are

Phosphate: 0.8–1.2%
Nitrate: 1.8–2.1%
Fluoborate: 0.8–1%
Zinc: 0.6–0.8%

The coatings generated would have weights that ranged between 0.4 to 1.2 grams per square foot, depending upon the type of alloy being processed (some aluminum alloys are considerably more reactive than others) and the period of time the article had been exposed to the phosphating bath.

Although these processing solutions were used for a mixture of metals, the aluminum part was always a problem, as it degrades the effectiveness of the baths. In amounts as little as 0.3 grams per liter, aluminum is able to keep steel from getting a zinc phosphate coating. As aluminum fluoride or sodium potassium aluminum fluoride salts are only very slightly soluble, the addition of excess fluorides is one way of extending the life of a mixed metal processing bath.[1] Another approach is to just use a no rinse processing bath and simply let the phosphate solution dry on the article. Another approach now used in many parts of the United States is a "closed loop" system in which very little, if any, of the processing chemicals are ever discharged into the environment, except those chemicals that remain on the articles. As stated earlier, phosphate systems for aluminum are only intended for paint adhesion. Recently, rare earth elements have been incorporated into the baths to improve corrosion resistance as they are quite inert, but the adhesion characteristics of the coatings suffer as a result.

Permanganates for Aluminum and its Alloys

Due to the fact that chromium is next to manganese on the periodic chart, there is a great deal of similarity between the two elements. As a result, the conversion coatings generated by permanganate solutions are quite similar

---

[1] Anchem Products, Inc. 1971. Brit. Pat. 1,324,460

in many areas, as shown by studies at Oxford University.[1] As in the case of hexavalent chromium compounds, the corresponding heptavalent valent manganese produced conversion coating system has the same mix of various reduced oxidation states on a given sample of aluminum. Both conversion coatings give much the same degree of corrosion protection. However, there are differences. The chromate-based system gives a water-based inorganic polymer, as does the permanganate system, but the chromate-based polymer is much thicker and better defined. As a result, the chromate-based system will give better corrosion protection, but the permanganate-based system will not decompose at temperatures of about 170° C. and, as such, may be used in powder coating applications. The paint adhesion characteristics of the permanganate-based systems are better.[2] With the exception of the high copper and/or high zinc alloys (2024, 7075 aircraft alloys, etc.), the corrosion characteristics are the same. To compensate for this deficiency, permanganate-based systems use a secondary seal to improve upon the corrosion resistance of aircraft alloys[3] and will meet the electrical contact resistance requirements. Permanganate-based systems will give a clear or a chromate yellow color to the processed light metals. Unlike the chromate-based conversion coating systems, permanganate-based systems may be easily stripped with a mild acid and a mild hydrogen peroxide solution. A new permanganate-based coating may be applied. Cold permanganate-based conversion coatings may be applied using spray on an entire aircraft without having to use a huge tank. Permanganates have been used for over 120 years to process potable water systems and are allowed in drinking water systems. Insoluble and very stable reduced manganese oxides are the only thing produced when permanganates enter a potable water system.

Synthetic Polymers for Aluminum and its Alloys

Up to this point, the conversion coating process has been presented as one or more strong oxidation processes that are applied to the metal. The metal in question is then very much a part of the conversion coating being generated. One example of this would be anodizing, where the conversion coating consists of the metal oxides or metal hydroxides. If it is sealed to obtain corrosion resistance, then the seal becomes a part of the conversion

---

[1] Danilidis, I. et. al., "Manganese-Based Conversion Treatment", University of Oxford, Oxford, U.K.

[2] Spadafora, S.J. 1992. "Naval Air Warfare Center Aircraft Division Warminster", Pa.

[3] Bibber, J. 1999. Corrosion 99, paper #491, NACE International, Houston

coating. If the seal you use is a chemical oxidant, such as chromates, you will generate chromate salts from the metal being conversion coated.

In order for synthetic polymers to attach themselves to the metal the polymer must have some kind of active acid or amine functionally that will allow the metal or its oxides to grab hold of the polymer. This will only occur if you have a very clean metal surface with a good oxidation reduction potential between the metal and the polymer in question. With the oxidation reduction potential of the light metals, water may well be sufficient to form a bridge that will help it to attach to the metal and the polymer in question. The problem is that in most metal finishing facilities it is not economically possible to get the metal clean enough to react with a polymer. Another alternative is to make the light metal the cathode in an electrochemical cell to force the reaction.

The "sol-gel" process involves the formation of various polymeric networks of metal oxides and/or silicon oxides to increase the paint adhesion characteristics of ceramic or glass surfaces.[1] Starting in the 1970s this process was studied extensively to prepare metal surfaces to better accept paints with a low temperature process that was developed to give inorganic gels for various transition metal (metals with atomic weights from ranging from 45.1 to 65.38) alkoxides and silicon alkoxides. This is referred to as the sol-gel process because a colloidal suspension ("sol") is first formed and then undergoes gelation ("gel") to form a unique inorganic network of transition metal oxides and silicon oxides.[2]

If properly prepared, the sol-gel is able to provide excellent paint adhesion and, in some cases, excellent corrosion resistance to a particular light metal alloy. The problem here is that the surface conditions of the light metal must be extremely clean to allow the sol-gel to attach itself strongly and, as such, it is not a viable process for the vast majority of metal finishing facilities. Once attached, the films are quite thin (50 to 100 nm), clear, and very difficult to detect without specialized equipment. Attaching silanes directly to an aluminum surface is also difficult due to the extreme degree of cleanness required and, once again, the processing is quite involved and tricky without having access to specialized equipment, which is often not found in the vast majority of metal finishing shops.

---

[1] Brinker C.J., and C. Scerer. 1990. "Sol Science," Academic Press, New York

[2] Filliagi, M.J. et al., J. Biomed Mat., 33:225; 1996

Naturally occurring gallotannin compounds and/or various sugar-based acids have been known to act as corrosion inhibitors. Attempts have been made to produce synthetic versions to act as corrosion inhibitors and paint adhesion agents.[1] They are only effective at precise pH and concentration levels and, as a general rule, will decompose at about 166 to 170° C. and, as such, are not very useful in powder coating applications. In many cases, these compounds are used in conjunction with zirconium, titanium, or hafnium compounds to obtain better paint adhesion and to prevent water staining on the aluminum, but an extreme degree of cleaning is required to insure the compounds actually attach to the metal. On average, the coatings produced by these compounds are not more than 10 nm thick.[2]

The rare earth elements, such as cerium, lanthanum, and yttrium, are indeed rare and, as a result, quite expensive. In addition, their oxides and/or hydroxides are quite unreactive and difficult to form on a light metal's surface as a gel, but they are often deposited as a barrier to provide for corrosion resistance on light metals like aluminum. On aluminum or magnesium, they are deposited as a clear film about 100 nm thick or a light yellow coating about 300 nm thick. The films are inorganic polymers held together by water molecules. When heated over 160° C., the polymer falls apart. To allow for more stability, various organic polymers are blended into the rare earths used as conversion coatings.

Cobalt compounds, which have been complexed with ammonia, will produce a barrier film of various cobalt oxides and hydroxides on a clean aluminum surface,[3] which is an inorganic polymer held together with water molecules in much the same way as chromate compounds. The barrier films generated are about 100 to 130 nm in thickness and clear. Thicker films are about 600 nm in thickness and yellow in color. Extensive cleaning is required for the films to attach to any of the light metals. Cobalt is expensive and there are many environmental issues associated with its use. The degree of corrosion resistance they produce is quite small. If properly applied, they will give good paint adhesion characteristics.

---

[1] U.S. patent, US4191596

[2] Lindert, A. and J.I. Maurer. "New Polymeric Materials for Metal Conversion Coating Applications", ACS Symposium Series, ISSN 0097-6156, 322 p. 209

[3] Carson, L.R. 1993. "Third Annual Workshop on Chromate Replacements in Light Metal Finishing", Albuquerque, N.M.; Sept. 15–16, 1993

Aluminum Hydroxide Conversion Coatings for Aluminum and its Alloys

The primary reason for the sulfuric acid anodizing of aluminum is to generate a hard scratch resistant surface that may be painted. The corrosion resistance of an anodized aluminum article is secondary in importance and is a result of converting the aluminum salts that make the anodized film into hydrated aluminum hydroxides that are then able to plug up the pores and thus provide for corrosion resistance. If good corrosion resistance is all you want, simply oxidizing the aluminum with water to form hydrated aluminum hydroxides should be sufficient, depending on how much corrosion resistance you want.

Aluminum is quite reactive, as it has an oxidation reduction potential relative to a standard hydrogen electrode of about -1.67 V., but it has an outer oxide film of about 4 nm or about 0.00000016 of an inch thick, which is quite effective at slowing down the normal oxidation processes and quickly reforms once it is removed. Boiling water is a good oxidant for pure aluminum, which will react within 30 seconds to give a film of hydrated aluminum oxides of about 0.00001 of an inch thick that also grows quickly and is easily reproduced. Give it another 5 minutes, it will only add about 0.00003 inch. It will not get much thicker than this; the maximum is about 0.00004 of an inch or about 1000 nm. This oxide coating is completely amorphous in structure and essentially the same kind of coating that forms when sealing sulfuric acid anodized films. The reported density of the hydrated films is 2.4 +/- 0.1 grams per cubic centimeter[1] and this compares well with the figure of 2.45 grams per cubic centimeter for hydrated aluminum hydroxides prepared by the hydrolysis of an aluminum salt in water solution at 95° C. with an alkaline salt, such as sodium hydroxide or aqueous ammonia.

Hydrated aluminum hydroxide film has the same density and, therefore, it may also be generated by simply soaking a pure aluminum panel in pure water at 40° C.; however, the films are twice as porous and may be easily be removed from the surface of the aluminum. The high temperature generated films will not part from the metal and seal the surface of the aluminum. In short, the aluminum hydroxide generated at 40° C. has a well-

---

[1] Bernard, W.J., Randall J.J., jr. 1960. Journal Electrochem. Soc.,107,483.

defined crystalline structure while the aluminum hydroxide generated at 100° C. is essentially amorphous in structure.[1]

None of this data was known in 1930 when Dr. Gustav Eckert developed a conversion coating process using a boiling solution of sodium chromate and sodium carbonate, which took about 3 minutes to generate a light to dark gray film on aluminum. This is called the "M.V.B." process.[2] What was also not known is that the water reacted with the aluminum first. This was then followed by the chromate, which further sealed up the surface of the aluminum. A number of related processes followed, all of which required boiling water as part of the process. Rather than adding all of the chemicals to the same pot and then bringing everything to a boil, the more recent "Sanchem 3000"[3] boiling water process is performed in stages and gives excellent corrosion resistance and adhesion characteristics.

1. Degrease, if necessary.

2. Deoxidize in a 10% nitric acid solution.

3. Rinse in D.I. water.

4. Place the aluminum article in boiling D.I. water for 5 minutes.

5. Immediately place articles in 1 % aluminum nitrate and 1 % alkali metal nitrate at 95–100° C for 30–45 seconds.

6. Rinse in D.I. water.

7. Place the aluminum article in potassium permanganate solution at about 60– 65° C for 3 minutes.

8. Rinse in D.I. water.

9. Place the aluminum article in potassium silicate solution at 90–95° C for 20–30 seconds.

10. Rinse and dry.

---

[1] Diggle, John W., Vijh, Ashok, K. 1976. "Oxides and Oxide Films", volume four, Marcel Dekker, pages 214 217.

[2] S. Wernick, R. Pinner and P.G. Sheasby. 1987. "The Surface Treatment and Finishing of Aluminum and its Alloys", Finishing Publications LTD, page 222.

[3] Bibber, J. U.S. patent, US4988396A

The initial boiling water process leaves excess aluminum hydroxides and smut from the aluminum alloy being processed. This is removed with the aluminum nitrate solution. The following potassium permanganate treatment builds the oxide film back up again and seals the gaps in the oxide film with reduced manganese oxides. The final silicate treatment quickly generates a top layer of aluminum silicate for maximum corrosion resistance and paint adhesion. In U.S. Navy testing, the process passed 336 hours of neutral salt spray (ASTM B 117) with no signs of corrosion on high copper and iron content alloys.

CHAPTER 4

ANODIZING

Anodizing brings about oxidation by making the metal the anode in an electrochemical cell. In other words, it is a method where one can generate a conversion coating on a given metal. All of the light metals may be forced to oxidize by the process, given the right electrochemical cell. Beryllium, magnesium, aluminum, and titanium are the only light metals that are commercially anodized to any great extent and the only ones considered here.

Beryllium

The standard method for anodizing beryllium goes back to a paper published in the *Trans Farday Society*[1] and has been used in one form or another ever since. The bath consists of 6 to 7 oz of chromic acid per gallon at 90 to 100 amps per square foot for about 30 minutes at 62 to 65° F. This will generate a dark gray to a jet-black oxide mixed with chromium oxides. The coating has excellent corrosion resistance and is quite slick and uneven. In 1963, a patent[2] was issued for a process where an alkali borate solution, containing 177 grams per liter sodium borate and 30 grams per liter of sodium hydroxide at 120° F., was used to generate a dark gray to jet-black coating that was not slick, but had well defined dimensions and went over 120 hours of constant salt spray with no signs of corrosion. It was also possible to generate multi-colored corrosion resistant oxide coatings using the bath. These are the only two anodizing conversion coating processes I have been able to find for beryllium.

---

[1] Levin, M. L. 1957. "Trans. Farday Soc., 1958, 54, 935–940" Dept. of Chemical Engineering, Imperial College, London, SW7, November 11, 1957.

[2] Pittman, Richard D. 1963. Northrop Grumman Guidance and Electronics Co., Inc. U.S. patent US3375179A.

Magnesium

Magnesium and its alloys may be anodized in much the same way as aluminum in order to provide a highly porous coating but magnesium oxide products are only useful for paint adhesion as they are soft, easily removed, and offer little, if any, corrosion resistance. The ease of removing magnesium oxides stems from the fact that they tend to be strongly alkaline and alkaline surfaces are very difficult to coat. The alloy content of the magnesium alloy you are working may improve the adhesion and/or corrosion resistance characteristics of your coating. A number of attempts have been made to improve upon the adhesion and/or corrosion resistance of anodized magnesium surfaces by adding borates, silicates, fluorides, phosphates, carbonates, organic acids, and chromates, with chromates having the greatest degree of success. Magnesium may be anodized in alkaline solutions or acid solutions. In alkaline solutions the typical alkaline formula for magnesium is as follows:

Sodium hydroxide: 240 grams per liter
Ethylene glycol: 70 grams per liter

With the addition of any one of the chemicals listed above in various amounts, the coatings end up being mostly magnesium hydroxide. The primary function of the coating is to improve paint adhesion. Magnesium may also be anodized using acids and the coatings produced will almost always have a composition that is similar to the following:

Ammonium bifluoride: 200 grams per liter
Sodium dichromate: 60 grams per liter
Phosphoric acid (85%): 60 ml per liter

With this formula, the resulting coating will consist of manganese phosphates, manganese fluorides, and various chromium oxides. Like the corresponding alkaline generated coating, this is quite porous and gives no corrosion resistance unless it is soaked in a dichromate solution for 30 minutes. The acid generated coating will stand up to heating without the loss of paint adhesion properties and its hardness is quite similar to anodized aluminum, but decreases with the thickness of the coating.

Aluminum

The outer oxide layer that naturally forms on aluminum and its alloys is quite thin (4 nanometers thick or about 1.6 of a ten millionth of an inch thick). You can increase that to about a hundred thousandth of an inch by placing a sheet of pure aluminum in boiling water, but you still have a very thin film of aluminum oxide. If you want thicknesses of about a thousandth of an inch or a ten thousandth of an inch, you have to force the issue by making the aluminum the anode in an electrochemical cell that has a stainless steel cathode, or another inert alloy or metal, in a strong acid, such as sulfuric acid. This process is referred to as "anodizing" and generally uses a sulfuric acid solution, although a number of other acids can be used.

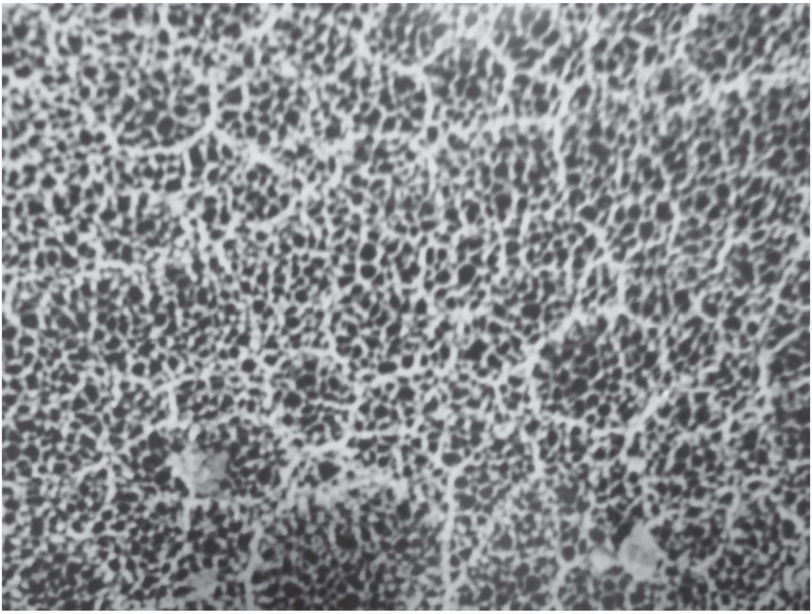


Figure 4.1 Naturally occurring aluminum oxide film; note the defined crystalline structure

Aluminum is the most widely anodized of the light metals at over a million tons a year. The primary reason for anodizing aluminum is to generate a hard, scratch resistant surface that will readily accept applied coatings. Aluminum generates this type of a coating because its chemistry dictates the formation of well-defined crystalline structures that are hard but also easily broken. As a result, anodized structures are not generally used in areas where they may be stressed, as this will cause the anodized film to crack or break, particularly if it is about 25.4 microns. In the industry, this is referred to as a "hard anodized" coating.

In almost all cases, about 15 to 20 % sulfuric acid is used as the electro-chemical anodizing bath for aluminum because sulfuric acid is a good oxidant and the least expensive of all the common mineral acids. The bath's temperature is maintained at about 20 to 25° C. to avoid the oxidized aluminum being dissolved into the electro-chemical anodizing bath. Depending upon the alloy being anodized, the voltage is maintained at about 15 to 20 volts. Direct current amperage is maintained at about 1 to 2 amps per square meter for 10 to 60 minutes to give average coating thickness values of about 3 to 35 microns. In the anodizing processes used, there no exact method as to how to process a given piece of aluminum. In many ways it is an art and a matter of "trial and error". As a result, each shop will have its own "trade secrets".

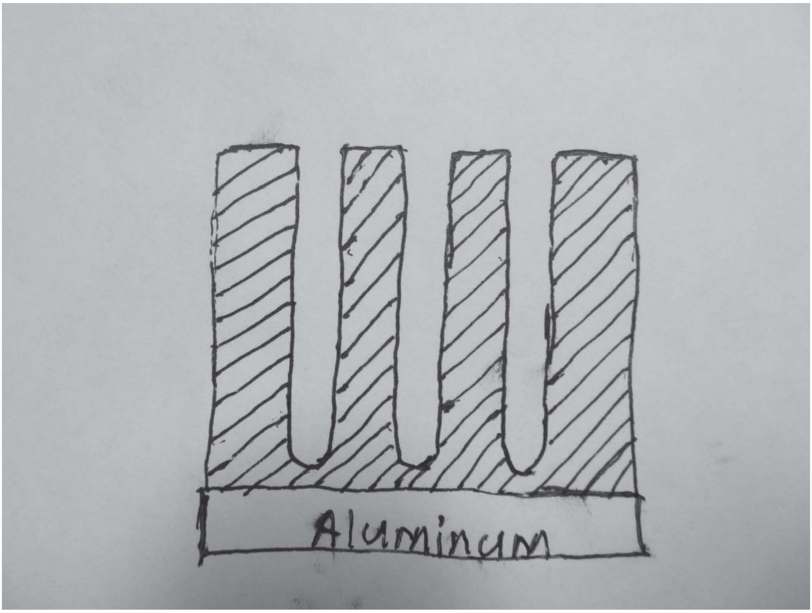


Figure 4.2: Cross-section of a freshly anodized aluminum surface.

An electron microscope photo of a cross section of a freshly anodized aluminum surface will show a thin bed of amorphous aluminum oxides just above the surface of the metal; this will comprise of not more than about 2% of its structure. Directly above this, it looks like there are stalks of corn, but these are actually the really well defined crystalline structures of various aluminum salts. A high percentage of the aluminum salts that comprise the "corn stalks" are aluminum sulfate and, in spite of extensive rinsing, one is never able to remove more than about 80 to 83 % of the sulfuric acid trapped within the coating. Additionally, if you were to force its removal, you would destroy the coating's structure.

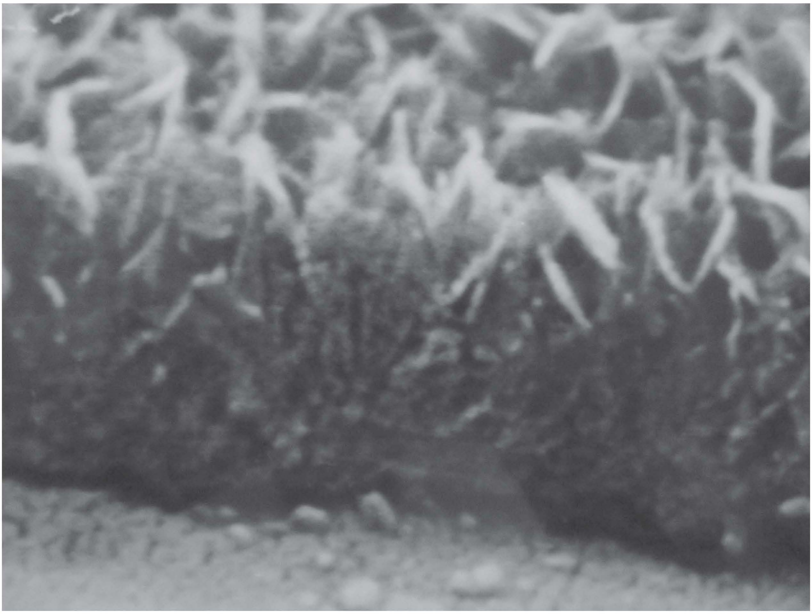


Figure 4.3: Amorphous aluminum oxide film generated by boiling water with approximately 0.00001 of an inch thick layer of aluminum oxide crystals on top.

If you are looking for good corrosion resistance, you need to "seal" the anodized coating. To do this, fill in the space between the so called "corn stalks" of various aluminum oxides and salts; the best process to complete this is still the boiling mineral free water process that began about 1940. At boiling point, or at least 95° C. (203° F.), there is a series of hydrated aluminum oxides that form, but if you have too high or too low of a temperature, they will not link together to form a good seal.[1] You either form a set of well-defined crystalline structures that will easily break and not adhere, or an amorphous non crystalline structure held together with water that will plug (seal) up the porous anodized structure. A number of other sealing processes may also be used, such as chromic acid, sodium

---

[1] Diggle, John W. 1976. Vijh, Ashok, K. "Oxides and Oxide Films", volume four, Marcel Dekker, pages 203–219

silicates, nickel acetate, and cobalt acetate. The United States Navy has adapted the use of a permanganate-based formulation as a replacement for chromate seals.

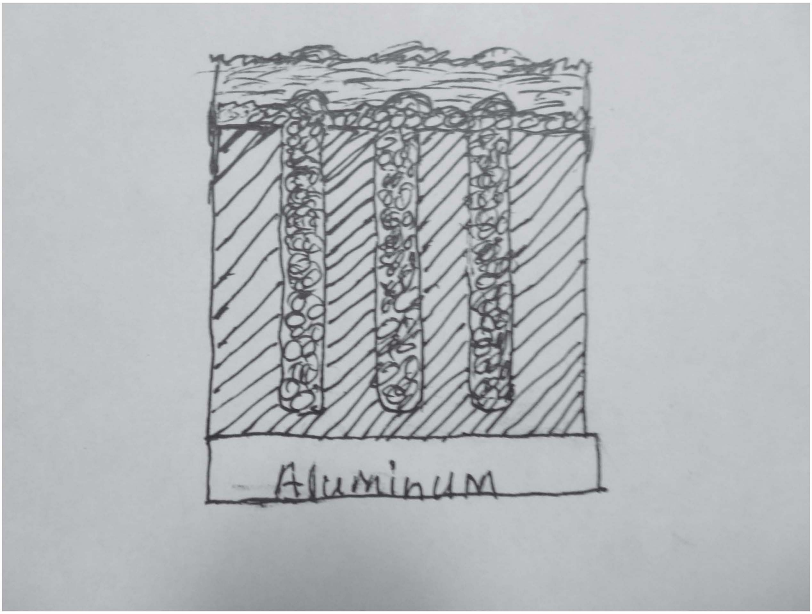


Figure 4.4: Cross-section of an anodized aluminum surface after being immersed in boiling mineral-free water for about half an hour; the open spaces are filled in with amorphous aluminum oxides.

Hot Water Sealing

More than anything else, the water that is being used needs to be as free of dissolved salts as possible. Use reverse osmosis or, if necessary, deionization. With pure water, the sealing process can start at temperatures as low as 80° C. Silica is a major poison and concentration levels even as low as 1 part per million will prevent the sealing process from taking place. In many parts of the world, ground water has a high silica content and its removal is an issue for aluminum metal finishing. Assuming you have very few salts in your water, the pH should be maintained at about 5.5 to 7.0l. Anything lower than a pH of 5.5 will not allow for effective sealing as the most important sealing component consists of various aluminum hydroxides that will not form at a pH that is lower than 5.5 or above 7.0. As it is almost impossible to keep sulfuric acid or sulfates out of the sealing water, try using a small ammonium acetate as a buffer to keep the pH at about 7.0, but do not use more than about 0.1%.

Place the articles to be sealed in the boiling water right after a through rinsing process and do not let the parts dry. Any previous drying will result in uneven sealing, with some areas not being sealed and other areas not having the anodized film properly adhered to the metal. Do not operate the sealing process for more than 30 minutes. If the part has not been sealed within 30 minutes, check on the quality of the water you are using or your rinsing procedure. Over 30 minutes in boiling water will result in poor adhesion of the anodized film to the metal surface and poor corrosion protection.[1] Having said that, it is also true that the most important factor in corrosion resistance is the alloy being processed. Alloys used in the aerospace industry will generally have a high heavy metal content that makes it very difficult to obtain uniform oxide coverage and, as a result, some areas of the alloy will be more reactive than other areas. Therefore, most aerospace alloys end up being sealed in a chromate or permanganate bath in order to have maximum corrosion resistance.

Steam Sealing

Sealing anodized coatings with steam has been used for some years in Asia and may be just as effective, if not more so, than water as there is a constant source of salt-free fresh water sealing the anodized surface. The most important aspect of steam sealing is the temperature; this should be about 100 to 110° C. Higher temperatures will result in driving off the water associated with the amorphous aluminum hydroxides that plug the pores in an anodized surface. Below 110° C., the steam consists of fairly large clusters of water molecules. If you go much higher than 110° C., you will start to form smaller clusters that will remove water molecules associated with hydrated aluminum hydroxide compounds.[2]

Steam sealing requires the use of more energy. This extra energy improves the efficiency and efficacy of the sealing process. As a result, 20 minutes will be sufficient to plug the pores (sealing). In addition, there are no issues associated with weakening the grip of the anodized film on the aluminum

---

[1] S. Wernick, R. Pinner, and P. G. Sheasby. 1987. "The Surface Treatment and Finishing of Aluminum and its Alloys", Finishing Publications LTD. P. 778.

[2] Diggle, John W., Vijh, Ashok, K. 1976. "Oxides and Oxide Films", volume four, Marcel Dekker, pages 203–211.

alloy. The steam process is more difficult to work with and requires steam cabinets that need to be free of air and maintained at the proper temperature.

Bloom Formation

It is all but impossible to prevent aluminum salts, such as aluminum sulfate, from being carried over into the boiling water or steam cabinet and then being converted into aluminum oxides or hydroxides. This means that it cannot be used in the sealing process. Instead, you will always end up with a thin film of oxides loosely attached to the anodized surface. This is referred to as a "sealing bloom". The best way to reduce the amount of bloom is to be as careful as possible in the rinsing process when coming out of the anodizing tank; however, this will only minimize the problem. It has been suggested that using 30% nitric acid will remove the bloom, but this will also weaken the hold the anodized film has on the base metal and decrease corrosion resistance. Other approaches to the problem have included adding phosphates to the water, but this will inhibit the sealing process.[1]

Chromic Acid Sealing

Chromic acid sealing has been used for decades by the military as the best possible method available to seal sulfuric acid anodized aluminum alloys with a high copper, iron, and/or zinc content as these alloys easily corrode in a marine atmosphere. The chromate penetrates down to the base metal, attaches to the metal, and forms an inorganic polymer of chromium. This does a very good job of sealing up the surface of the metal and keeping salt and other corrosive agents away. The chromate does not plug up (seal) the open pores generated by the sulfuric acid anodizing. The filling in of the pores occurs when the water in the bath is maintained at a pH of about 6.0 to 8.0 and at a temperature of about 95 to 100° C. The baths generally contain about 15 to 20 grams of potassium dichromate per liter and potassium or sodium hydroxide can be added to get the 6.0 to 8.0 pH needed. The sealing time is about 20 to 30 minutes followed by a rinse in mineral free water.

---

[1] S. Wernick, R. Pinner and P.G. Sheasby, 1987. "The Surface Treatment and Finishing of Aluminum and its Alloys", Finishing Publications LTD., pages 799–800.

Potassium Permanganate Sealing

Due to the fact that chromates are known to be cancer-causing agents, chromate-based sealing has been replaced by the military with a permanganate-based process. In many ways this is quite similar to the chromate-based process. The freshly anodized aluminum articles are rinsed in mineral free water and then placed in the permanganate-based seal at about 170° F. for about 15 minutes, and then they are rinsed and dried. The articles have an initial pink color that fades to a dark brown. The sealing is due to the pores of the anodized surface being sealed off with amorphous reduced manganese oxides rather than the aluminum oxides, as the temperature is only about 170° F. The corrosion resistance every bit as good as in chromic acid-based sealing.[1]

Nickel and Cobalt Salt Sealing

Nickel hydroxide is quite heavy relative to aluminum hydroxide; it has a density about twice that of aluminum hydroxide. It is very amorphous and has a light apple green color. It is quite effective at sealing up the pores of any anodized aluminum surface. It is absorbed into a given aluminum anodized surface as nickel nitrate or nickel acetate and then hydrolyzed and precipitated as hydroxide. Cobalt salts may also be used. After sealing, the article often goes through the hot water sealing process to improve the seal. When dying an anodized article, the nickel may react with an organic dye to generate a new metal complex. The seal is not as corrosion resistant as sealing with steam or hot water.

Silicate Sealing

The use of silicate sealing began in 1931 and so it predates hot water and steam.[2] At the time, not much work, if any, was performed on sealing anodized articles as a result of hydrating the aluminum oxides or aluminum salts. Silicate, as mentioned earlier, is a potent inhibitor of hydration in aluminum and its salts. As a result, a large portion of aluminum salts are

---

[1] Berman, Elizabeth, Mason, Robert B. 2017. "Reducing Chromium plus six in Military Anodizing Operations", Products Finishing, volume 81/No.5, February 2017, pages 17–19.

[2] Dunham, R.S. 1931. British Patent 393, 996.

converted into aluminum silicates and any free acids will react to generate silica and plug up the pores.

The baths have a ratio of about 1 part potassium oxide to 4 parts silicon dioxide or 1 part sodium oxide to 3 parts of silicon dioxide in order to have excess silica available to fall out of the solution and plug up the pores. Using a one to one ratio has no sealing effect. The respective sealing solutions are about 5 % solids and operated at about 95 to 100° C. for 30 minutes after which the oxide film's attachment to the metal starts to weaken. The silicate sealing gives a permanent bloom on the treated articles, which is impossible to remove. The processed articles are resistant to alkaline attack, but not to acid conditions. In 500 hours, use ASTM B 117 neutral salt spray to test the results; however, this is not as good as chromate sealed panels, but it is slightly better than hot water and just as good as cobalt or nickel sealing processes. All testing was completed using the high heavy metal alloy "2024" used in aerospace applications, which was not clad with pure aluminum.

Aluminum: Phosphoric Acid Anodizing

Like sulfuric acid, phosphoric acid is quite inexpensive and environmentally friendly. It is used in anodizing is for paint adhesion or adhesion. Unlike sulfuric acid generated salts that are then hydrated, phosphoric acid generated films are, more or less, resistant to hydration and have more attachment points in the form of fine whiskers, as well as a very fine porous structure.[1] In addition, aluminum is often anodized in phosphoric acid to improve the adhesion of the metals electroplated.

The typical phosphoric acid bath consists of about 20% phosphoric acid maintained at a temperature of about 20 to 30° C. with a current density of 0.7 to 1.8 amps per square meter at a voltage of 10 to 50 volts, depending upon the application. It is anodized for between 5 to 20 minutes. In some cases, sulfuric acid is added to the bath to modify the structure of the anodized film to suit the needs of the end user in terms of adhesion characteristics.

---

[1] Venables, J.D., McNamara, D.K., Chen, J.M., Sun, T.S. and Hopping, R.I. 1979. Applications of Surface Science, 3, 88–98.

Oxalic Acid Anodizing

Oxalic acid anodizing was used from the 1940s until the early 1960s. If it was used with sulfuric acid, it produced a gold or black hard coating that could create films of up to 0.002 of an inch or 0.005 cm. The basic process had current densities of 1.5 to 2.0 amps per square meter and a from 50 to 60 volts. The bath was maintained at 20 to 25° C. with treatment times of 50 to 70 minutes. The coating has a larger pore size than sulfuric anodized coatings, a thicker barrier layer, and larger cell size. The oxalic acid concentration ranges from 5% to 12%. Adding 1 to 4 % oxalic acid to your standard sulfuric acid anodizing bath will give a hard black anodized film.

Titanium

Titanium has a naturally formed layer of various oxides that make the metal and its alloys rather inert to attack, but which may be oxidized when made the anode in an electrochemical cell under alkaline or acid conditions. Thickening the outer oxide layer allows greater paint adhesion. The oxides may become thickened due to the various colors that can be formed by various mixed metal oxides generated; this depends on the applied voltages.

Titanium may be anodized on the acid or the alkaline side. A Boeing patent[1] is operated on the acid side to improve adhesion properties, while a patent issued to Theodore M. Pochily[2] operates on the alkaline side.

---

[1] Yukimori Moji, J. Arthur Marceau, Boeing Co., U.S. Patent: US3959091A.

[2] Theodore M. Pochily Worthington, E. Parker, U.S. Patent: US3338805A.

CHAPTER 5

HEAVY METALS CONVERSION COATING SYSTEMS

Most heavy metals are elements that very much want to lose electrons. That is to say, the metals want to oxidize and the greater the ease of losing electrons, the more metallic the element. There are now about 118 elements in the periodic chart and about 77% of these elements, or 91 of them, are metals. We cannot discuss all of them in terms of conversion coatings because a large number are quite rare and have essentially no practical uses in industry or develop little or no outer layer of oxides; therefore, it is all but impossible for them to generate or make use of a conversion coating.

Vanadium is the first of the so-called heavy metals as it is has a density greater than 5. It is relatively rare and difficult to oxidize; therefore, it has no real need for a conversion coating. The same may be said for chromium and manganese, both of which are primarily used to modify the properties of iron and other related elements. Cobalt and nickel are rare elements that are rather corrosion resistant and develop little in the way of an outer oxide coat. Iron is the only element here that needs one or more different types of conversion coatings for greater adhesion or corrosion resistance. Conversion coatings for copper and silver are also included.

Iron

The earth's core is almost entirely made of iron and, as a result, it comprises about 4.7% of the earth's crust. Iron is only second to aluminum in terms of abundance, but it is much easier to extract from its ores as most iron oxides are good oxidizing agents. As a consequence, iron oxides will quite easily react with reducing agents, such as carbon, to generate the free element, which explains why elemental iron has been known to man for at least 3,000 years.

There are 3 common iron oxides found in nature. Hematite is the deep red or brown ore that is associated with water. It is the most common ore and composed of 3 oxygen atoms and 2 iron atoms with a plus three oxidation state, which is the most stable oxidation state. Magnetite is the second most common ore and it is composed of 4 oxygen atoms and 3 iron atoms; it has 2 iron atoms in a plus 3 oxidation state and 1 iron atom in a plus 2 oxidation state. The least common of the ores is siderite, which may come in a number of different colors ranging from gray to light yellow, depending on what is contaminating it. It is the least common of the ores as it consists of 1 iron atom in a plus 2 oxidation state and 1 molecule of carbonate ion.

Iron Based Conversion Coatings

Iron Oxides

Iron prefers to be in the plus 3 oxidation state, which explains why hematite is the most common iron ore or iron oxide. Iron needs water, which is a good oxidant, to initiate the formation of hematite by creating iron hydroxide; this is then easily converted to hematite in the presence of free oxygen. Hematite has no ability to adhere to the surface of the iron and is easily removed, thereby allowing more corrosion to take place. If you have somewhat restricted access to free oxygen, you will end up with a layer of magnetite under the outer layer of hematite which will slow the oxidation process, but it will not stop it entirely as it has some ability to adhere to the surface of the iron.

Magnetite or black iron oxide is mostly generated for cosmetic reasons as it is easily removed and affords little corrosion resistance. Quite often the outer film of magnetite is coated with a thin film of wax or oil to allow for corrosion resistance, which will increase the salt spray (ASTM B117 standard) corrosion resistance from a few hours up to between 21 to 160 hours, depending upon the type of oil or wax being applied.

There are a number of different methods used to generate a magnetite film on iron or steel and all of them are dependent upon the kinetics (the rate or change in the direction of a chemical reaction depending upon the energy being applied to the reaction in question) of the reaction to produce a suitable magnetite film. As we have already mentioned, simply putting a piece of steel in a wet or humid atmosphere will cause it to form hematite or red rust. If you use steam at high temperatures, you will get the black magnetite instead due to the kinetics of the reaction. The high temperatures place limits on how much oxidation can take place in a given period of time and how much contact may take place with a given molecule of water. The steam process will also produce a significant amount of hydrogen while forming the magnetite. A more commonly used process, but much more dangerous, is placing the iron or steel article in sodium or potassium hydroxide solutions at boiling point. As in the case of the steam approach, kinetics are at work. This process does nothing to produce magnetite at room temperatures, but, at boiling point, there are limits on how much water may come into contact with the article in any given period of time. As a result, only the black magnetite oxide has an opportunity to form rather than any of the other oxides. One of the earliest methods for producing magnetite goes back several centuries, when iron or steel was dipped in melted potassium nitrate to retard corrosion in cannons. It also improved the iron and steel's properties by forcing nitrogen into them, which increased their hardness and/or strength. Today, the process is used in "nitriding" or forcing nitrogen into iron or steel to increase its hardness. Chromates may also be used to generate magnetite, along with a film of reduced chromium compounds, by placing the iron or steel article in a boiling solution of sodium or potassium chromate. This will provide a significant amount of corrosion resistance but, due the toxicity of the treatment solution, it is no longer used.[1]

Iron Phosphate

The oxides of iron and/or its alloys will do little or nothing to enhance adhesion or to increase corrosion resistance unless sealed with waxes, oils, and chromates. Phosphates are used to increase adhesive characteristics and/or improve corrosion resistance. This is instead of molecules consisting of iron and oxygen, which give us magnetite, hematite, and siderite. Now, we generate compounds with similar structures, but we use phosphate ions in place of the oxygen atoms. We have not done away with iron in its plus 3 oxidation state and, as a result, we still get well defined crystalline structures instead of an inorganic polymer held together with water molecules or an amorphous "mud". As a consequence, iron phosphates will still do little more than allow good paint adhesion.

The use of simple iron phosphates (there are 3, as phosphoric acid will react with 1, 2, and/or 3 atoms of iron, but only the phosphate attached to 1 iron atom is added to the processing bath) goes back to Roman times, even though they did not have any idea about what they were actually doing. And here we need to once again make use of kinetics to exercise control over the rate of the chemical reactions used to obtain good paint adhesion and/or some degree of corrosion resistance. Any given phosphating bath will be

---

[1] https://doi.org/10.1002/bbpc.19580620615

modified to take the iron alloy into consideration. In addition, the bath will constantly change as the chemicals are used up or modified by reacting with the iron alloy. The iron articles to be processed may have the iron phosphate bath wiped, sprayed, or used as a dip. The dip process will give the most consistent results and control over the quality of the resulting coating. The typical iron phosphate coating will range in coating mass from about 0.25 to 1.1 grams per square meter (0.000152 cm; 0.00006 of an inch) to about 0.00152 cm (0.0006 inch) or thicker. The baths may be at an ambient temperature up to about 65° C. The ambient temperature baths are generally operated from 30 to 90 minutes with agitation. Faster times come from using higher temperatures or adding oxidants to the bath. The coatings range color from yellow for the thinnest of coatings to dark blue black for the thickest of coatings. The pH of the baths generally range from 4.0 to 6.0, with a pH of about 5.0 being optimum. At a pH of 4, the coatings tend to be dusty, which is probably due to too much oxidation giving a high degree of iron plus 3 phosphate in the conversion coating. At a pH of 6, the coating tends to be loose, which may be a result of iron oxides rather than iron phosphates getting into the coating.

As might be expected, slow iron phosphating gives large iron phosphate crystals and better paint adhesion. Faster phosphating gives smaller crystal formation and more corrosion resistance, but the corrosion resistance never gets that high. Over the past few years, several manufactures have started adding rare earth elements to their phosphating baths as they have a strong tendency to be rather inert. This has somewhat increased the corrosion resistance, but the rare earth elements are quite expensive and the improvements have been minor.

In any metal treatment process, the most important factor is the cleaning process. If there is any rust on the steel or iron parts, hydrochloric acid will remove it but, at the same time, the acid will activate the metal to increase the oxidation. After removal of the rust, quickly rinse off the acid and clean in a strongly alkaline cleaning solution as this will passivate iron and its alloys. Avoid silicated cleaners, as they will cling to the surface of the metal and are difficult to remove. As a result, it is difficult to activate the iron or iron alloy to accept phosphate-based coating. After alkaline cleaning, quickly rinse and then use hot air to quickly dry the parts as water rusts iron and its alloys.

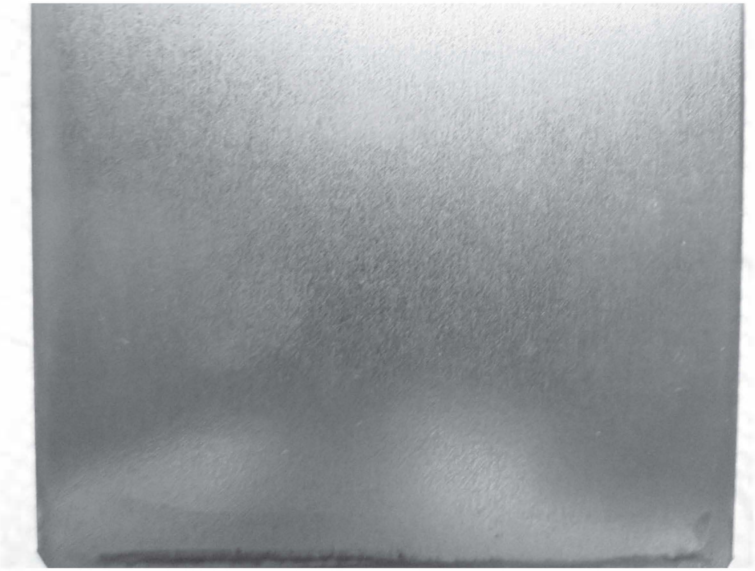


Figure 5. 1 Iron phosphate over steel variation; the gray color is a result of variations in the thickness of the manganese phosphate.

Zinc Phosphate

Zinc phosphating iron and its alloys are used because they (only one phosphate molecule is attached to one zinc atom in the baths used) react faster and give smaller crystals. They generate a film of zinc oxides or hydroxides that have a strong tendency to form inorganic polymers held together with water molecules or an amorphous "mud". In other words, you should get better corrosion resistance. The coating is white from the formation of various zinc oxides and zinc hydroxides. It reacts about 3 times faster than the iron phosphates and will be attacked by strong acids or alkali as the zinc compounds will dissolve. Essentially, all the other characteristics, as outlined in the iron phosphate section, remain the same.

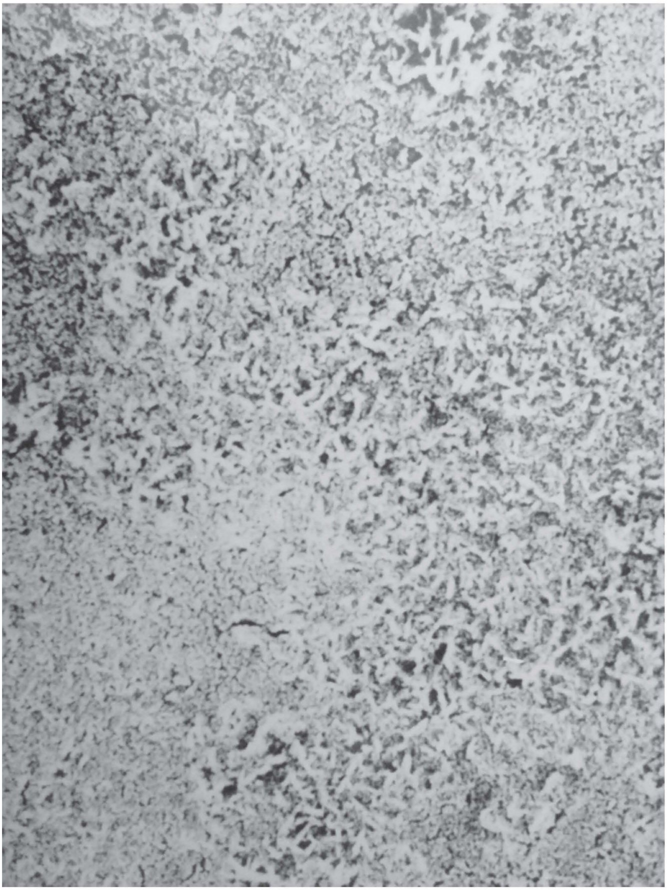


Figure 5. 2 Zinc phosphate showing its fine crystalline structure.

Manganese Phosphate

Manganese phosphating of iron and its alloys is used because manganese phosphate (which only has 1 phosphate molecule per manganese atom) gives a very hard and scratch resistant coating. The baths are operated at about 95° C. for 5 to 20 minutes. Other than that, the process is not that much different than when generating iron phosphate coatings.

Hot Dip Zinc Coated Iron and its Alloys

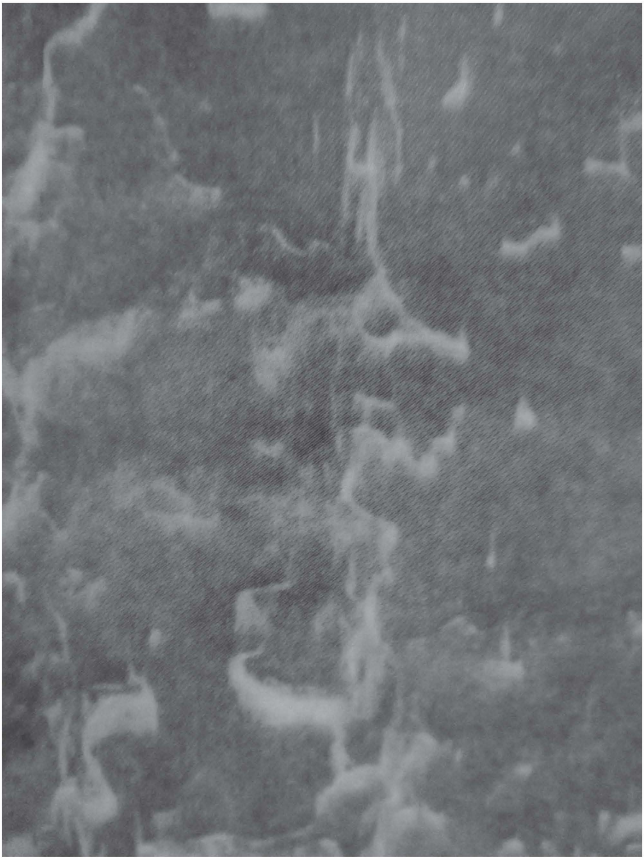


Figure 5.3 Hot dip zinc over steel or electrodeposit then melt; both give no porosity.

Zinc has been coated on iron or related alloys (e.g., steel) ever since the process started in 1836. This was called "galvanizing" by its inventor, Sorel. It is coated by dipping the iron or related alloys in the melted zinc (melting point of 419.5° C.). The iron or related alloy will then resist rusting as the zinc, being in direct contact with iron or its alloys, sets up an electrochemical cell that causes the zinc to more easily corrode then the iron or related alloy. If the coating is rather thick (more than 0.003 cm or 0.001 inch), the zinc will act as though it is not attached to the iron and its alloys but, in most cases, the applied zinc coating is much thinner due to the cost.

It also has a stronger reactivity. Thinner coatings of zinc are generally applied through an electrochemical cell consisting of zinc chloride or related zinc salt in an acid bath or, in some cases, an alkaline bath. Nearly half of all the zinc produced today is used in plating steel. The huge increase in the use of zinc plated iron and its alloys may be directly traced back to 1980 when cadmium was branded as an environmental poison. Up until then, cadmium was the preferred material to prevent corrosion on iron and its alloys.

Plating Zinc on Iron and its Alloys

Acid plating is generally used because it is less expensive, but the deposit tends to be stiffer and not as uniformly distributed over the surface of the substrate. This occurs because larger individual particles of zinc form before they are able to attach themselves to the metal being plated. In addition, it is very difficult to prevent the oxidation of iron and/or its alloys under acid conditions, which results in non-uniform deposits. With alkaline zinc deposition, the zinc particles are smaller when they attach to the metal and the plating process is slower and more uniform in coverage as iron and its alloys are passive under alkaline conditions. In other words, little or no oxidation of the iron or its alloys will take place during the plating process.

Conversion Coating Processes for Zinc Coated Iron and its Alloys

Conversion coating processes for zinc have been in use since about 1920 and there are a number of different processes. The 4 primary conversion processes in use are

(1) Chromate-based processes using chromates or the application of trivalent chromium compounds that then revert to chromate. The most stable oxidation state for chromium is the plus 6 state.

(2) The production of a precipitated film of heavy metal phosphates.

(3) The use of various synthetic or naturally occurring polymers.

(4) The formation of various manganese oxide/zinc oxide films using permanganate based conversion coatings.

Cleaning Zinc Coated on Iron and its Alloys

Zinc is a very reactive metal that may be attacked using both acids and the alkali to remove dark and difficult oxides and/or hydroxides of zinc deposits. First, degrease if necessary, and then clean with a simple nonionic cleaner. The outer oxide film is removed with a 30 to 60 second dip in a strong alkaline cleaner; rinse in mineral free water; dip in a 1% nitric acid solution to remove all traces of alkaline residue; and then give a final rinse in mineral free water. If the zinc is electrodeposited, it is normally conversion coated immediately to prevent the reformation of zinc oxides or hydroxides. Electrodeposited zinc is sometimes heated to drive out any trapped hydrogen. This should be done before cleaning and conversion coating the zinc.

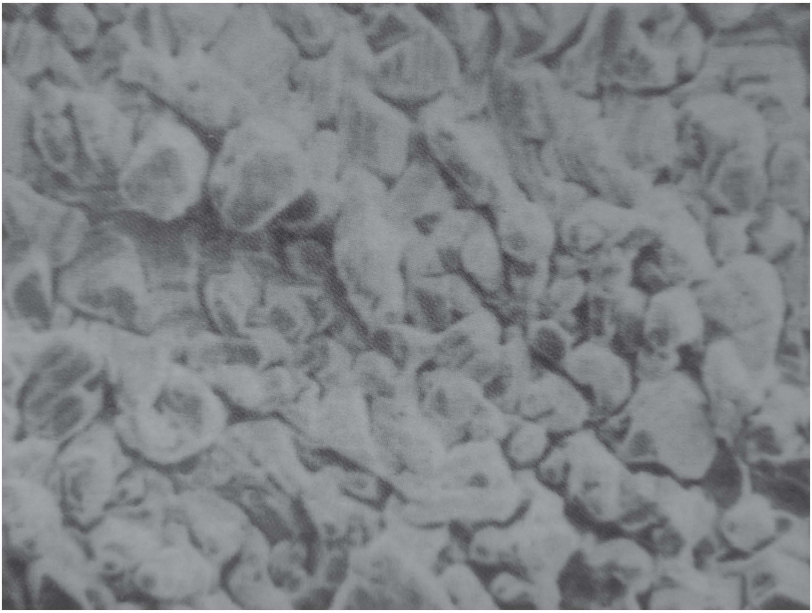


Figure 5.4 Zinc electrodeposited on a steel surface, which gives it an open and porous structure.

Chromates on Zinc Coated Iron and its Alloys

Chromates, like zinc, have a strong tendency to form an inorganic polymer held together by water molecules and, as a consequence, they are quite effective on zinc. A number of different conversion coating processes, based upon chromates, are used on zinc and its alloys to provide corrosion resistance. Very light or colorless chromate-based conversion coatings are produced by using a pH of 0.0 to 1.5 (at low pH levels or high hydrogen ion concentrations; individual chromate ions are in the majority). These coatings will have a mass pf about 20 mg per square foot or about 215 mg per square meter and a coating thickness of about 80 to 100 nm. They are widely used in the electronic industry and provide protection against humid or wet conditions, but give little or no protection against a salt atmosphere. Colored chromate conversion coatings are produced by solutions with a pH of 1.0 to 3.5, due to their much lower hydrogen ion concentrations and, as a result, we then have chromate ions associated with each other in short polymers. As expected, these solutions generally provide the best corrosion protection. They have a thickness of about 200 to 300nm and a mass of about 40 mg per square foot or about 430 mg per square meter. They have low electrical resistance and are an excellent paint, base assuming you paint within 8 hours. After 8 hours, an inorganic polymer of gel forms, making it difficult to paint the conversion coated zinc. They will also give some degree of salt spray protection in addition to its excellent resistance to high humidity or wet conditions. The most corrosion resistant of the chromate conversion coatings on zinc are the ones that are applied anodically in a pH range of 2.5 to 6.0. They are most frequently used in the aviation industry and give a black coating or a transparent coating if used in the refrigeration industry. The color will depend on the applied voltage. The zinc oxides mixed with the chromate gel give a harder and more dense coating. The coatings will pass extended salt spray tests and are the most corrosion resistant of the chromate generated zinc conversion coatings. Once again, chromate-based coatings will lose their water of hydration at about 170° F. or about 76° C., which makes them all but impossible to powder coat. Chromium plus 3 conversion coatings are difficult to apply and quickly convert themselves to the hexavalent form once out of the treatment bath. In many cases, a dye is added to keep invisible the yellow color characteristic of chromate-based conversion coatings.

Heavy Metal Phosphates on Zinc Coated Iron and its Alloys

The use of heavy metal phosphates (iron, manganese, zinc, and chromium, etc.) is the oldest process for conversion coating zinc and its alloys and gives the best possible results in terms of paint adhesion. Zinc phosphating solutions will, in almost every case, contain some form of zinc phosphate as the major component of the bath in order to control its activity and about 1.3 to 1.5 as much iron in order to help drive the phosphating reaction. The coating thickness will average about 1000 to 2000 nm but may run as high as 6000 nm. The most difficult of the zinc alloys to phosphate are the zinc aluminum alloys, as aluminum is a negative catalyst to the phosphating reaction. Where these alloys must be phosphated, fluoride is added to the bath to precipitate the aluminum as aluminum fluoride. The presence of iron in will cause deposits to show up on the surface of the zinc and lead to galvanic corrosion, making a poor corrosion-resistant conversion coating even less corrosion resistant. As such, all zinc phosphating baths will result in some degree of pitting that traps and holds unwanted heavy metal deposits (essentially iron), salt, water, and so on; this further decreases its corrosion resistance.

All zinc phosphate conversion coating baths require a significant amount of monitoring to keep the pH and/or the concentration of the chemicals within a very narrow range. In addition, the baths have a high rate of chemical use. Zinc phosphate baths are generally operated at about 135° F. (57° C.) to 155° F. (68° C.) for about 70 to 130 seconds, which will give coating masses of about 120 to 920 mg per square foot or 1.29 grams to 9.90 grams per square meter.

Permanganate and Organic and Inorganic Polymers on Zinc Coated Iron and its Alloys

Manganese sits to the right of chromium on the periodic chart and it is extremely similar to chromium in and so permanganate is quite similar in its chemistry to chromate. The same may not be said for vanadium, which sits to the left of chromium. The simple positive ions of vanadium are not stable in contact with water and its chemistry is essentially the same as a non-metallic elements. In addition, vanadium is much more expensive and has several toxicity issues associated with its use.[1] On the other hand, permanganate has been used to purify potable water systems for over a hundred years and is allowed in drinking water all over the world. Thus, the conversion coatings produced by permanganate are, as expected, quite similar to the coatings produced by chromates without the associated toxicity issues.[2] As in the case of hexavalent chromium conversion coatings,

---

[1] https://www.atsdr.cdc.gov/ToxProfiles/tp58-c3.pdf

[2] Danilidis, I., 1998. et. al., "Manganese-based Conversion Treatment," Dept. of Materials, University of Oxford, U.K.

the heptavalent manganese generated conversion coatings contain an almost identical set of reduced metal oxides.

Just as chromium plus 6 oxides are reduced to lower valence chromium hydroxides and/or oxides, so too are the higher valence manganese oxides reduced to lower valence manganese hydroxides and/or oxides. The manganese generated conversion coatings also produce an inorganic polymer held together with water molecules, but the polymer is not nearly as strongly held together. As a consequence, the corrosion resistance may or may not be as good as a chromate-based system, but heating the permanganate generated conversion coating will not cause it to decompose as easily as the chromate-based systems, and other inorganic or organic polymers may be added to obtain similar or even better corrosion resistance. Thus, permanganate-based conversion coating systems may be used in various powder coating systems where chromates cannot be deployed, as they will not be able to stand up the high temperatures used in powder coating operations.

Permanganate based conversion coating systems will not allow zinc to form difficult to paint over hydrophobic films of zinc hydroxides and/or zinc oxides. By itself, permanganate will form a conversion coating on zinc that will provide as much corrosion protection as a thin (100nm) chromate-based conversion coating over galvanized steel.[1] This may be improved through the use of a secondary organic seal that chemically bonds to the permanganate generated conversion coating, while still allowing for good electrical contact resistance as the conversion coating is still quite thin. In addition, the system does not require an excessively clean surface and the polymer itself lifts off any attached "dirt". The gold brown conversion coating has about 0.5 mg per square foot or 5.38 mg per square meter and is about 20 nm thick. Its characteristic color allows for a quick check to see if the conversion coating has formed properly. If the conversion coating has not formed properly, it may be quickly and easily stripped and conversion coated again if necessary. A clear version is also available that uses a non-synthetic inorganic polymer system (about 0.1 mg/square foot or about 1.1 grams per square meter) with a thickness of about 10 nm and an easy to use system to quickly check of the conversion coating has formed properly. The entire conversion coating process takes about 60 seconds.

---

[1] Biestek, T. and J. Weber. 1976. "Electronic and Chemical Conversion Coatings", p. 74, Portcullis Press Ltd., Redhill, Surrey, U.K.

Coil Coating Processes on Zinc Coated Iron and its Alloys

All of these processes may be modified to allow for the conversion coating of zinc coated iron and its alloys on a continuous strip of coated metal, although not all are used in coil coating processes. The strip to be conversion coated is generally cleaned in an alkali solution, rinsed with low mineral content water (about 15 to 20 ppm solids), cleaned again in a mild mineral acid solution to remove the outer oxide layer and any traces of alkali, rinsed again in low mineral content water, and then the excess water is removed with a squeegee to prevent any dilution of the applied conversion coating. In many cases, fumed silica is mixed with the conversion coating to enhance the paint adhesion characteristics to give an average wet film thickness of about 10,000 to 13,000 nm and a dry film mass of about 17 to 24 mg per square foot or about 210 mg per square meter. In another approach, various synthetic or natural organic polymers are used in place of the fumed silica, which is dependent upon the coating that will be finally applied to the zinc coated iron and its alloys. The polymer thickness is generally 3,000 to 5000 nm thick with a dry mass of about 13 to 15 mg per square foot or about 150 mg per square meter. The strip is then usually heated to about 120° F. (50° C.) before the application of the final coating to enhance the drying of the applied conversion coating. In some cases, the strip is etched by the applied conversion coating to generate zinc ions, which then become part of the conversion coating and increase its hardness and corrosion resistance. In all cases, the primary goal of coil strip conversion coating processes is good paint adhesion.

Tin Coated Iron and its Alloys and Conversion Coating the Product

In chemistry, metal has always been defined as an element that wants to lose its outer electrons and the greater the ability of a given element to lose electrons, the more metallic it is. As a result, there has always been an argument over its designation. When pure, tin cooled to about 13° C. becomes a gray or white solid as a result of forming well defined diamond shaped crystals that do not release electrons or conduct an electric current. When warmed up, the process reverses itself, but tin still persist in forming diamond shaped crystalline structures. As a result, tin is often referred to as a "semimetal" or a "metalloid" as defined by the Oxford Dictionary. To prevent tin from forming a fine gray dust it is alloyed with trace amounts of lead, bismuth, and antimony; therefore, commercial tin is only about 99.8% pure. It should also be noted that tin will dissolve in strong acids and/or strong alkali. In both cases, highly hydrated tin oxides are generated, which clump together and form a protective barrier over the tin. Chromates have been used as protective conversion coating systems since the 1920s.

The element melts at about 232° C. and will easily stick to iron surfaces. Tin was first used to make tin cans in the early 19th century by simply dipping the iron article in the melted tin; this method continued into the early 20th century. As tin is much more expensive then iron and its alloys, dipping soon gave way to using an electrochemical cell of tin chloride or tin hydroxide to apply films that are now only about 0.0001 of an inch thick.

In the application process, a low carbon steel is used to obtain better adhesion characteristics and the strip of steel being coated is flipped over during the plating process to ensure that both sides are plated with tin. The strip is then rinsed, quickly heated to the melting point of the tin, sprayed with a chromate-based conversion coating, rinsed, dried, and finally sprayed with a thin coating of lubricant and rolled up. The lubricant has an average thickness of about 0.0000002 inches. The conversion coating is on average about 0.0000003 inches thick (for tin deposits of 0.0001 of an inch) and designed to resist sulfide staining and to improve the corrosion resistance of the steel, as tin thicknesses of only 0.0001 of an inch (0.00025 cm) are little more than decorative. You need tin thicknesses of at least 0.001 of an inch (0.0025 cm) to get a good corrosion resistance on iron or its alloys.

The conversion coating used has been based upon chromates in one form or another. Going back to the 1920s, chromating solutions were acid, but became alkaline in the 1940s as the coatings had little or no color associated with them and were excellent at resisting stains due to sulfur containing foods. In addition, chromates can be applied by making the tin plate the cathode in an electrochemical process that deposits small amounts of pure chromium and/or various chromium oxides. Sulfide stain testing of the protective value of the conversion coating is generally done with a cysteine hydrochloride in water solution adjusted to pH of 7.0 with a phosphate buffer. The test is run at the boiling point of the water for 20 minutes. Chromates are a well-known cancer-causing agent and attempts to get around their use have centered on trying to use a plastic coating on the inside of the cans, but this is a more expensive process and many can producers have returned to the use of chromates. Another approach is to use an alkaline permanganate-based conversion coating system.[1]

---

[1] United States patent application, US20150050518A1

Copper Oxidation

Copper and its alloys are fairly inert with regard to oxidation to begin with and, in many cases, the oxidation process is performed for purely cosmetic reasons. Copper is little effected by alkaline solutions, but will be attacked by a number of acids. As a consequence, most, if not all, intentional oxidation of copper takes place under alkaline conditions.

The copper or copper alloy article is first degreased and then cleaned in a mild ammonia solution as this will dissolve and cupric (plus 1 oxidation state copper) salts. Once cleaned, the articles are made the anode in an electrochemical cell that consists of a stainless steel cathode and a sodium or potassium hydroxide water solution of at least 150 grams per liter at 85 to 95° C. at a current density of about 0.7 amps per square meter. If you are processing a brass or bronze article, the temperature should be maintained at about 65 to 70° C. in order to prevent the oxidation of the tin (bronze) or the zinc found in the brass articles. The time of treatment is generally 25 to 35 minutes. Initially the deposit consists of cuprous oxide (copper in the plus 1 oxidation state), which is a light yellow color but, as the process continues, there will be increasingly less copper that is not oxidized. At some point, the outer layers of cuprous oxide begin to oxidize to the black cupric (plus 2 oxidation state) oxide which does not adhere nearly as well as the cuprous oxides. The coating will no longer increase in thickness and you will start to see a deposit of greenish copper hydroxide.[1] Copper and its alloys may also by oxidized without the use of an electric current to make the article an anode. What is generally done is to add a strong oxidizing agent to a strongly alkaline solution. Hydrogen peroxide is not stable under alkaline conditions. So, placing the article to be oxidized in a 5 % potassium hydroxide solution and then slowly adding hydrogen peroxide will quickly generate free oxygen that will create the desired oxide coating. After oxidizing the articles in question rinse them in hot and cold water, dry in hot air, and then apply a thin film of wax or oil. For every liter of 5% potassium hydroxide add about 1.5 grams of hydrogen peroxide.

---

[1] D.W. Shoesmith, S. Sunder, M.G. Bailey, G.J. Wallace, F.W. Stanchell, "Anodic Oxidation of Copper in Alkaline Solutions: Part IV. Nature of the passivating film," Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 143, issues 1–2, 1/10/83, P. 153–165.

Conversion coating silver

Silver is conversion coated for one reason only, it will develop a dark gray black coating of silver sulfide due to sulfides found in various foods (e.g., eggs) or in the air from the decomposition of organic matter or natural gas sources. Another source of staining is chlorine or other halogens. To this day, the primary method used to prevent the dark stain found on silver is to conversion coat it with a chromate of one kind or another, despite the fact that they are known cancer causing agents. At one time chromic acid was used by itself to avoid anything that would cause anything more than a slight reaction with the silver. This generated a very thin protective film of hydrated chromium oxides and silver chromate. An alternative approach is to make silver react with an alkali metal dichromate at a pH of about 3.5 for about 15 minutes at about 20 to 30° C. This should be followed by a rinse in mineral free water and a dip in boiling water[1] to produce a harder hydrated film of chromates.

Another approach to create "stain free silver" is to make the article the cathode in one or more dichromate solutions. Making the silver the cathode increases the reactivity of the silver toward the chromates in the bath and gives a thicker film. The baths used generally contain from 100 to 200 grams per liter chromate at about 2 to 3 amps per square meter and at a voltage of about 5 to 6 volts for 40 to 140 seconds at an ambient temperature. As might be expected, there is an improvement in the stain resistance of the silver whether the articles are placed in boiling water or not. In all cases, the testing involved soaking the silver article in a 5% solution of sodium sulfide at an ambient temperature for 5 minutes.

An alternative to the use of chromates involves an alkaline permanganate solution as outlined in US patent application: US2015005051814. The treatment solution chemically reacts with the silver and seals the surface of the silver article.

---

[1] Keil, A., Metalloberflache. 1957. 11,44.

CHAPTER 6

CONVERSION COATINGS FOR PLATING METALS

Plating Aluminum and its Alloys

Aluminum and its alloys will quickly generate a thin protective film of non-amorphous aluminum oxides once exposed to the air after alkaline cleaning or a dip into an acid deoxidizer. In addition, the oxides will not form in an even and regular pattern due to the alloyed elements. As a consequence, this is not a good surface for the deposition of another metal as some areas of the aluminum will have heavy deposits of oxides, while others will have high concentrations of the alloyed elements. In an attempt to minimize this, plating shops working with aluminum, or other light metals, install one cleaning or deoxidizing bath after another in a futile attempt to produce a surface that is as free of oxides and/or alloyed elements as possible. The more tanks that are installed, the more expensive the process.

The first attempts to improve the plating of aluminum and its alloys involved finding a metal that could be easily deposited on aluminum and its alloys. The deposit was used to prevent or slow down the formation of aluminum oxides and to set up a fairly even electrochemical cell over the article that would attract and hold other metals on the surface. One of the more successful processes was by B. Vogt in the 1920s, which plated a thin film of zinc on aluminum. As in the case of many metal finishers of the time, Vogt had little formal education in chemistry and developed his process by trial and error. It was a long and involved process but, at the time, aluminum was a rather expensive element and it did work. The process, as outlined below, illustrates the complexities involved to process aluminum in the 1920s.[1] This centered on cathodic cleaning at about 7 volts for 3 to 5 minutes at an ambient temperature in a caustic solution of sodium hydroxide, sodium cyanide, and sodium carbonate.

---

[1] Wallbank, A.W. J. 1952. Electrodepositors Technical Soc. 28, 209.

1. Rinse for about three minutes in mineral free water.
2. Acid clean in equal volumes of concentrated sulfuric acid and concentrated nitric acid at an ambient temperature for about 3 to 5 seconds.
3. Rinse for about 3 minutes at an ambient temperature in mineral free water.
4. Cathodic cleaning again in a sodium cyanide, sodium hydroxide solution at 7 volts for 20 to 30 seconds at an ambient temperature.
5. Rinse for about 3 minutes at an ambient temperature in mineral free water.
6. Electrodeposition of zinc from strongly alkaline, low zinc concentration bath (about 0.5 grams per liter) containing sodium cyanide at an ambient temperature for about 20 seconds at about 0.5 amps per square meter.
7. The deposit will be quite thin and have a bronze color if properly processed. The article is then quickly rinsed and immediately placed in an ambient temperature brass plating bath (mixture of a zinc salt and a copper salt under alkaline conditions) for about 8 to 10 seconds at about 0.8 amps per square meter to give a very thin brass deposit with a pale yellow color. Anodes of 70/30 brass are used in the process.
8. The articles are then quickly rinsed with mineral free water as the deposits are very thin and subject to oxidation.
9. The articles are now ready to be nickel plated in a bath of nickel sulfate 250 grams per liter; magnesium sulfate 100 grams per liter (improves conductivity); sodium chloride 5 grams per liter (maintains an active metal surface); or boric acid 25 grams per liter (maintains an active surface). The plating is carried out with a current density of about 1.5 amps per square meter at a pH of 5.6 at about 46° C.
10. Rinse in mineral water.
11. The article is then heated for half an hour at 230° C to insure a good adhesion of the elements and to check the quality of the nickel plating. If you do not have good adhesion, the plating will blister.

This zinc plating process continued to be used for some time, although a number of modifications were made to shorten the process.[1] However, the most important factor is that zinc was identified as the element needed to set up an electrochemical cell on aluminum surfaces, which would allow other metals to be plated using aluminum and its alloys. Later, chemical methods that did not depend upon the application of an external electrical source were found[2] and these processes are known as "zincates".

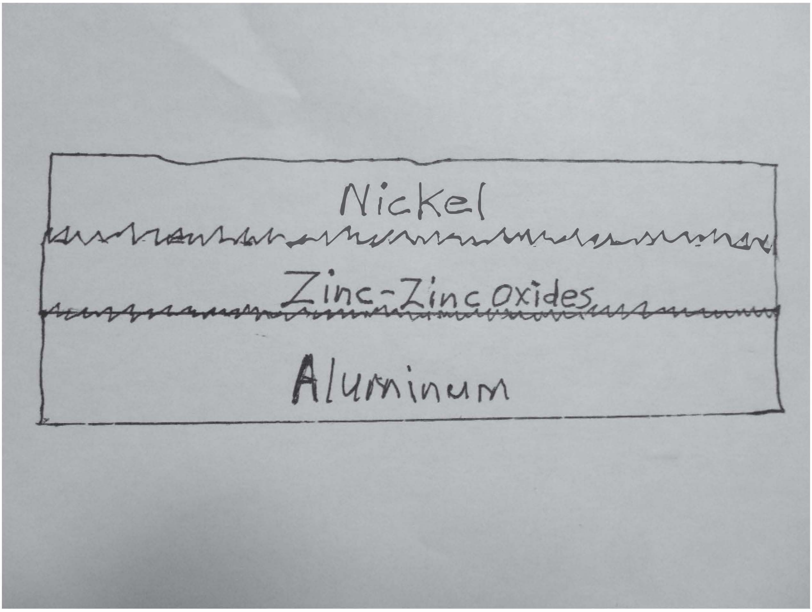


Figure 6. 1 Cross section of aluminum, which has been zincated and nickel plated.

Zinc metal will be attacked and dissolved with a strong alkali or acids. The metal is referred to in the literature as being "amphoteric". That is to say, it may form ions both as an acid and as a base. On the alkaline side, zinc will react with either sodium or potassium hydroxide by first forming a neutral zinc hydroxide which is attached to 2 hydroxyl ions. Adding more sodium or potassium hydroxide will dissolve the zinc hydroxide to produce zinc which is attached to 4 hydroxyl ions and has an overall -2 charge. The resulting solutions are referenced as "zincate solutions" and are generally

---

[1] Edwards, J. and Swanson, C. J. 1953. "Trans. Institute Metal Finishing". 29, 209.
[2] Hewitson, E. H. 1927. (Eastman Kodak), U.S. Patent 1,627,900.

generated from sodium hydroxide and zinc oxide. On the acid side, zinc or zinc oxide will be dissolved by mineral acids, generally hydrochloric acid to give zinc salt with a zinc ion. This is associated with 6 water molecules and a formal plus 2 overall charge, but aluminum is not chemically active enough under acid conditions (aluminum is more easily oxidized under alkaline conditions) to allow the zinc to be reduced by the aluminum. Aluminum is also "amphoteric" but, under alkaline conditions, it is generally free of any protective oxide films and will much more easily give up 2 electrons to a zinc ion and thus acquire a coating of elemental zinc. However, if the "zincate solution" is too alkaline, it will result in the aluminum being dissolved by the alkalinity before any plating can take place. Therefore, alkaline "zincate solutions" are generally maintained at a pH that is not more than about 12.5. Most zincate solutions are made by dissolving about 40 to 50 grams of zinc oxide in 400 to 450 grams of sodium hydroxide. Above or below these limits, the adhesion will be too weak or the coatings too thin.[1]

Since the initial development of standard zincate solutions, numerous variations on the basic formula have been published and patented to improve upon the adhesion or thickness of the zinc deposit. However, the most important factor continues to be the initial cleaning and oxide removal steps, which will vary depending upon the composition of the aluminum alloy you are working with. In all cases, the most important factors will be how much zinc actually attaches to the aluminum or aluminum alloy, and the uniformity of the zinc deposit. The uniformity and bonding of the zinc is dependent on how well the aluminum is cleaned. A typical cleaning sequence is as follows:

1. Vapor degreasing or emulsion cleaning.

2. Alkaline cleaning, try and avoid silicated cleaners as silica tends to tightly adhere to aluminum. In fact, phosphate or carbonated cleaners give the best results.

3. Rinse in mineral free water.

4. Acid etch, which will depend upon the alloy.

5. Double rinse in mineral free water.

---

[1] Petrocelli, J.V. 1950. "J. Electrochem. Soc.," 97, 10; 1951, 98, 183; 1952, 99, 513.

6. Immersion in zincate solution.

7. Rinse in mineral free water.

8. In many cases, it is desirable to use a dip in a 50% nitric acid solution for a few seconds to remove unwanted oxides and loosely adhered zinc, rather than the aluminum.

9. Rinse in mineral free water.

10. Second dip in the zincate solution for about 30 seconds.

11. Triple rinse in mineral free water.

12. Place directly into the plating bath (nickel, copper, silver, or chromium).

As indicated by this long series of processing steps, there has not been much improvement since the 1920 B. Vogt method.

Tin is considerably more expensive then zinc and it is also much less easily corroded. It is deposited on aluminum, or its alloys, to improve the electrical conductivity, facilitate soldering, and to provide a lubricated surface on aluminum and its alloys. This process originated in the 1930s.[1] It can also be deposited on aluminum and its alloys by non-electrical chemical processes.[2] This process has been used since the 1940s and it is known as the "stannate" process because tin used to be called "stannis" and its chemical symbol is "Sn". The typical "stannate" solution and processing steps consist of the following:

1. Degrease, if necessary.

2. Etch at an ambient temperature for about five minutes in a 5% potassium hydroxide solution.

3. Rinse in mineral free water for about 90 seconds.

4. Dip parts in an acid solution of 5% ammonium bifluoride, 25% concentrated sulfuric acid, and 80% concentrated nitric acid for about 5 minutes at an ambient temperature.

---

[1] Brown, M., Schulburg, V. and Dell, G. 1936. Automotive Ind., 75, 884.

[2] Krammer, O. 1945. "Metal Industry", 66, 121.

5. Rinse in mineral-free water.

6. Plate by immersion in a 150 gram per liter solution of potassium stannate solution at about 50°C for 1 minute.

7. Rinse in mineral-free water at an ambient temperature.

There are a number of variations on the above basic formula. In addition to being an excellent lubricant for aluminum and its alloys to improve electrical conductivity and facilitate soldering, tin also sets up an electrochemical cell with aluminum and its alloys; this allows the aluminum article to be coated in tin. Due to the fact that tin is a rather inert element, the corrosion resistance of the aluminum, as well as the metal, will be improved.

Intentional Oxidation of Aluminum for Plating

A number of plating processes for aluminum and its alloys have been developed. These are based on intentionally building up the natural protective oxides on the surface of the aluminum to generate an adhesive film for the plated metal to hold onto. An anodized aluminum surface is sealed with an organosilicon compound or a potassium silicate solution and then baked at about 250° F. for 30 minutes, cooled and then coated with a thin film of an inert metal, such as tin, gold or palladium. This sets up a strong electrochemical cell to allow the article to be plated with copper when dipped in a 3% alkaline copper sulfate solution. The outer oxide film holds the copper in place.[1] Another example involves using a 4% oxalic acid solution as your anodizing bath followed by an acid etch to open up active sites or generate small pits in the aluminum to allow it to be plated.[2] The vast majority of anodized and plated aluminum articles come from anodizing with a phosphoric acid solution. This is because phosphoric acid etching gives a rather thin oxide film that allows for easier access to the solution.

Electroless Nickel Plating on Aluminum and its Alloys

The autocatalytic deposition of nickel or electroless nickel is an immersion process that does not need an external source of current to cause the nickel to deposit itself on the article. The catalysis that initiates the plating process,

---

[1] Zimmerman, J. 1967. (Sperry Rand Corp.) U.S. patent 3,340,164.

[2] Travers, W.J. 1931. U.S. Patent 1,971,761.

in the vast majority of applications, is an article that has gone through a zincate immersion process or other types of catalysis, such as stannate immersion. In the case of zincate coated light metal articles, we have an electrochemical cell (zinc in direct contact with a light metal, such as aluminum) that initiates the oxidation reduction process. For aluminum, the type of zincate solution used has a strong influence on the adhesion characteristics of the nickel deposit because the thinnest zinc rich deposits give the best overall results.[1] In all cases, a small percentage of the reducing agent (hypophosphite, borohydride, or borane) will end up becoming alloyed with the nickel deposit to a small degree. In the case of sodium hypophosphite, (the most widely used reducing agent) your deposit will end up having phosphorus in it. The higher the phosphorus content, the harder and more scratch resistant your deposit. In the case of sodium borohydride or dimethylamine borane, you will end up having boron in your nickel deposit. The higher the boron content, the harder and more scratch resistant your nickel deposit.

The electroless process is non-directional. When using an external current source, you must have your electrochemical cell's anode pointed at the cathode where the deposition will take place. It is very difficult to get a uniform deposition on the article you are plating and, if you have, for example, deep screw holes, it will be all but impossible to get deposits into the recessed areas. In addition, electroless deposition will not attack the metal being plated. Electroless deposition will, in most cases, release hydrogen and deposition will not take place in areas where the hydrogen cannot easily escape. In many cases, electroless nickel deposits can be made as hard as chromium deposits with much less expense and fewer toxic chemicals. Typical applications include pumps, gears, and hydraulic cylinders.

The first electroless nickel baths were used and patented by Brenner and Riddell, who worked at the United States National Bureau of Standards. They were designed for use on steel, but worked just as well on aluminum and other light metals.[2] Almost all of the electroless nickel baths for aluminum and its alloys are based upon sodium hypophosphite and this was the reducing agent that Brenner and Riddell used in their studies. They are operated in a pH range of about 4.0 to 6.0, temperature range of 85 to 95° C. (bringing the bath to the boiling point is generally not a problem), and have a nickel content of about 4.0 to 8.0 grams per liter. The ratio of nickel

---

[1] Mallory, G.O. 1985. "Plating and Surface Finishing", 72, No. 6, 86.

[2] Brenner, A. and Riddell, G.E.J. 1946."J. Research Nat. Bur. Stand. 37, 1–4.

to sodium hypophosphite is of some importance for the stability of the bath and for the phosphorus content of the deposited nickel alloy. The ratio is generally maintained at about 3.13 grams of sodium hypophosphite to each gram of nickel. The phosphorus content of the deposit ranges from about 3% to about 12%, with 3% being at the soft end of the deposits (a density of 8.65 grams per cubic cm) to 12% at the high end (a density of 7.85 grams per cubic cm). Pure nickel has a density of about 8.91 grams per cubic cm. The softer deposits will provide greater corrosion protection as they are less porous, while the harder and more brittle deposits will be scratch resistant and more porous. In all cases, you will need at least 0.001 inch of thickness or 0.0025 cm to get any significant corrosion resistance. Additionally, deposits of less than 0.001 inch or 0.0025 cm are referred to as "decorative deposits". Most deposits on aluminum and its alloys contain about 6% phosphorus with a density of about 8.33 grams per cubic cm.

In the early development of electroless nickel technology, the baths tended to be somewhat unstable and did not have that long a life. To solve that problem, a few parts per million of lead were added to stabilize them. Adding too much would cause the baths to just shut down and too little would leave them unstable. Due to the toxicity of the lead, organosulfur compounds and related organic compounds are now added in parts per million amounts which, like phosphorus, tend to become part of the deposit and may have an effect upon the porosity and density of the deposit. Another source of stability comes from the pH used. As a general rule, the higher the pH, the more unstable and reactive the electroless bath. Another set of issues related to the stability of the baths is the presence of any stray nickel or dust particles. The baths need to be constantly filtered of residue to maintain their stability. Related to this is the issue of the use of zincates and/or stannates. They are not uniform in reactivity because some aluminum alloys are very reactive, while others are slow to react. As a result, the zinc or tin, and the aluminum oxides are not uniformly distributed over the articles to be processed. Aerospace aluminum alloys with high copper, iron, and zinc content, which is distributed in an irregular pattern over the surface, generates stability and/or deposit problems. At the other end of the spectrum, marine grade aluminum alloys, which are designed to be relatively non-reactive, will have rather slow deposition rates.

The bath life of the processing solutions, assuming they are properly filtered, is measured in "bath turn overs" or the number of times you are able to replenish the nickel and reducing agent. The literature on the subject states that you should be able to get 8 "turn overs", but a lot of that depends upon what alloys you are working with which will, in turn, affect the uniformity of the zincate or "stannate" coatings and the effect of the alloyed elements. In addition, the composition of the bath is an issue. At one time, working baths contained the nickel salts from various organic acids, such as hydroxylacetic acid, which was quite effective at stabilizing the nickel. Today most, if not all, of the nickel additive is nickel sulfate, as this is much less expensive then organic acid salts, but by the time you get to 8 turn overs, your bath is very ionic and loaded with sulfate ions that inhibit the plating process[1] and cause instability. In point of fact, the residue zinc and/or tin building up has an adverse effect on your bath life and contributes to your waste disposal issues.

Non-Zincate or Stannate Process

All of the approaches discussed so far involve generating an electrochemical cell on the aluminum or aluminum alloy that starts and continues the deposition process. Generating the irregular mixed zinc or tin deposits and the associated metal oxides requires a lot of processing tanks, as well as a lot of expensive labor. Additionally, once the nickel alloy is deposited on the metal and on top of the layer of assorted metal oxides, it makes it easy to generate a crack or hole or for a blister to develop due to the release of hydrogen from the debris field of oxides.

The new approach[2] involves:

1. Degreasing, if necessary.

2. Cleaning it by making the article the cathode in a 5% potassium hydroxide in a water solution electrochemical cell for about 15 to 20 seconds.

3. Rinsing in mineral free water.

4. Making the article the cathode or the anode in a dispersion of various amino acids and amines for about 2 to 3 seconds.

5. Rinse off excess amines and amino acids not chemically bonded to the article with mild ammonia in a water solution.

6. Rinse off any excess ammonia solution.

---

[1] Mallory, G.O., J.B. Hajdu. 2009. "Electroless Plating: Fundamentals and Applications", A.E.S.F. p. 72–74.

[2] Bibber, J.W. 2013. Sanchem, Inc., U.S. patent US8388826B2.

7. Place the article in the hypophosphite electroless nickel bath.

At this point, the extremely thin film of amino acids and amines is being slowly displaced out into the nickel bath and being very quickly replaced by the deposited nickel. You may observe the more reactive areas of the article reacting first and then spreading to the less reactive areas. The reaction is a little slow and will take about 10 minutes (the reaction time depends upon the alloy in question) after which you will observe the uniform and even release of hydrogen from the article. A cross section of the article as observed in an electron microscope photo clearly shows that there is no layer of metal oxides. The only things present are the aluminum alloy layer, which is directly followed by the hypophosphite generated nickel. The option to deposit the amino acids or amines by making the article the cathode or anode relates to the type of finish you want, as making the article the cathode results in a slightly more porous and decorative coating. It should also be noted that you do not need to go directly into the nickel bath. You can just dry the processed article and put it in a clean, dry area. The article now has a protective film and will not generate an oxide film. When you want to process the article, just soak it in warm (about 30° C. or 86° F.) mineral free water for about 5 minutes. It should be noted that baths which do not use hypophosphite as a reducing agent may also be used. The amount of amino acids and/or amines that are displaced into the bath are quite small and will have little or no effect on the plating process or the bath life. The vast majority of the plating on aluminum and its alloys are directly or indirectly related to the plating of nickel in one form or another. This process may also be used as a catalysis for the deposition of other metals, such as copper, as it does give good results.

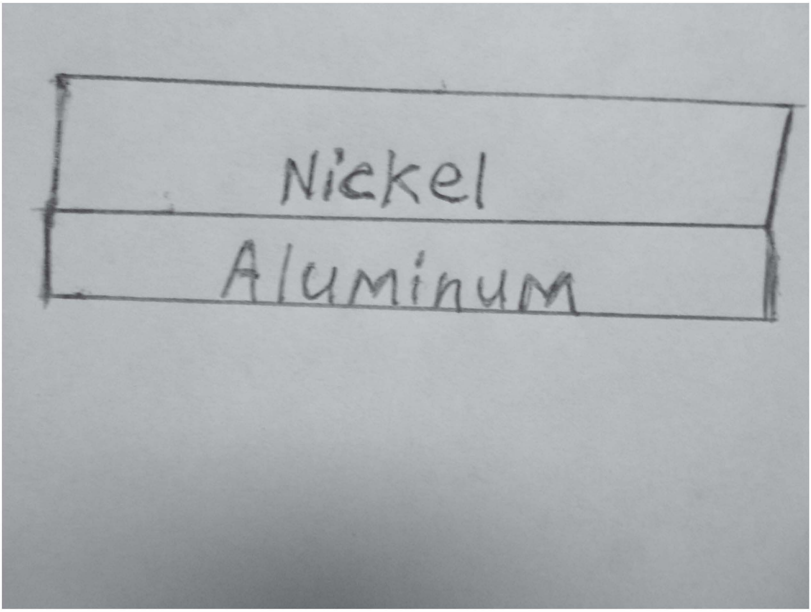


Figure 6. 2 Cross section of aluminum plated with nickel after being coated with an organic polymer.

Plating Beryllium

As indicated in the section on beryllium and conversion coatings for adhesion and corrosion resistance, beryllium is quite toxic and its outer layer of oxide is very difficult to remove and replace with a more corrosion resistant conversion coating. The same issues follow beryllium into the plating arena. Once again, we have to revert to the use of a zincate or acid-based zinc salts to deposit a thin film that will then set up an electrochemical cell to allow for the deposition of other metals. Copper (-0.34 V. relative to a standard hydrogen electrode) is a more noble element than nickel (+0.25 V. relative a standard hydrogen electrode); therefore, depositing a film of copper on the beryllium first will improve your ability to deposit nickel. It will also increase the chance that the copper will enhance the beryllium's ability to oxidize before it can be nickel plated or after the nickel has been applied. Unless the copper has been deposited in a rather thick film, you can expect to find oxides just waiting to be covered over with electroless nickel.

One of the more generally accepted cleaning and deposition methods used with beryllium is as follows:

1. Degrease, if necessary.

2. Make the beryllium the cathode in an electrochemical cell consisting of a 5 % potassium hydroxide solution in water and a stainless steel anode for 30 seconds at an ambient temperature.

3. Rinse in mineral free water.

4. Etch in concentrated nitric acid containing 1% ammonium bifluoride at an ambient temperature for about 30 seconds.

5. Rinse in mineral free water.

6. Immediately alkaline the zincate for 60 seconds.

7. Rinse in mineral free water.

8. Strip the zincate for 30 seconds in a concentrated nitric acid.

9. Rinse in mineral free water.

10. Alkaline the zincate for 30 seconds.

11. Rinse in mineral free water.

12. Copper strike in a cyanide copper electrochemical cell bath.

13. Rinse in mineral free water.

14. Perform the hypophosphite electroless nickel process.

15. Remove, rinse in mineral free water, and hot air dry.

Beryllium: Non-Zincate Processing

An alternative to the zincate-based process of generating an electrochemical cell on the surface of a beryllium article is as follows:[1]

1. Degrease, if necessary.

---

[1] Bibber, J.W. 2013. Sanchem, Inc., U.S. patent US8388826B2.

2. Make the article the cathode in an electrochemical cell consisting of a stainless steel anode and a 5% potassium hydroxide water solution for 30 seconds at an ambient temperature.

3. Rinse in mineral free water.

4. Etch the article in concentrated nitric acid containing about 1 % ammonium bifluoride.

5. Rinse the article in mineral free water.

6. Make the beryllium the anode in a slightly alkaline dispersion of various polyamino acids and amines in an electrochemical cell with a stainless steel cathode for about 2 to 3 seconds at an ambient temperature.

7. Rinse excess polyamino acids and amines with a mild ammonia solution in water.

8. Rinse the excess ammonia with mineral free water.

9. Place article in a 20% copper sulfate solution containing 5 grams per liter concentrated sulfuric acid and 1% ammonium bifluoride at an ambient temperature for about 10 minutes to develop a uniform and even copper flash all over the article.

10. Rinse in mineral water at an ambient temperature.

11. Place the article in a hypophosphite based electroless nickel bath.

12. Remove, rinse, and dry.

The outer protective film of polyamino acids and amines are only removed when the article is in the "electroless nickel" bath and dispersed into the plating bath.

Plating Magnesium

There is a great deal of industrial interest in magnesium because it has about the same tensile strength as aluminum (1.738 grams per cubic cm), but is only about 64.37 % as heavy as aluminum (2.70 grams per cubic cm.) It is also more brittle than aluminum, but that problem can be solved with proper alloying. The alloy "AZ31B" is one of a number of the more ductile types available but continued working of any alloy will cause them to "stiffen up". Magnesium alloy names are often 2 letters followed by 2 numbers. Letters indicate the main alloying elements (A = aluminum, Z = zinc, M = manganese, S = silicon, and B = bismuth). The numbers indicate the percentages and start with the first element. So "AZ31B" would be 3% aluminum and 1% zinc and a fractional amount of bismuth. For more exact percentages, consult the manufacturer. Most, if not all, of the alloys manufactured in the United States contain at least 1% aluminum.

As indicated in the earlier section on conversion coatings for corrosion resistance, magnesium and its alloys are generally easily oxidized and, unlike beryllium and titanium, the oxides are not strongly attached to the surface of the metal or alloy. As a consequence, the surface of most of these alloys and metal have an alkaline (pH of 10.0 or higher) reaction to moist pH paper, which makes it very difficult to deposit any metals or organic coatings (e.g., paint). One way to get around this is to add a lot of fluoride to your processing solutions because magnesium fluoride is both hard and extremely insoluble in water.

The more or less present zincate industrial process for plating nickel onto magnesium is indicated below. At present, there are only a few shops in the entire United States that will plate magnesium and its alloys and there is about a 20% rejection rate due to blistering, cracking, and so on, which is due to the nickel deposit. As indicated earlier, the oxidation-reduction potential relative to the standard hydrogen electrode is about + 2.34 volts and the current process involves the deposit of a rather thick film of copper directly on the magnesium or its alloy. This makes for a very good "battery" and any moisture that is trapped in this system will generate a lot of hydrogen gas. Strong alkaline conditions will passivate magnesium and its alloys.[1]

1. Soak in a strong alkaline cleaner at 180 to 200° F. for 3 to 5 minutes.

2. Rinse in mineral free water at an ambient temperature.

3. Use chromic acid or phosphoric acid to remove as much free magnesium oxide as possible for 30 to 60 seconds.

4. Rinse in mineral free water at an ambient temperature.

5. Use phosphoric acid (85%) as a fluoride etch for 1 to 2 minutes

---

[1] Dow Chemical Company. U.S.A. 1982. Inorganic Chemicals Dept. *Operations in Magnesium Finishing*.

6. Rinse in mineral free water at an ambient temperature.

7. Use the acid fluoride, zincate, at 160 to 165° F. for 3 to 5 minutes.

8. Rinse in mineral free water at an ambient temperature.

9. Use the copper-cyanide strike at 130 to 140° F. for 6 to 8 minutes.

10. Rinse in mineral free water at an ambient temperature.

11. Place in a fluoride hypophosphite-based electroless nickel bath to the desired thickness.

12. Rinse in mineral free water at an ambient temperature, then dry and bake at 450° F. for an hour.

Organic Zincate Free Process[1]

1. Degrease, if necessary.

2. Make the magnesium or magnesium alloy the cathode in an electrochemical cell consisting of 5% potassium hydroxide in a water solution and a stainless steel anode. Allow the article to release hydrogen for about 30 seconds.

3. Rinse in mineral free water at an ambient temperature.

4. Make the article the anode in a polyamine acid and polyamide dispersion electrochemical cell with a stainless steel cathode for about 2 to 3 seconds.

5. Rinse off the excess polyamino acids or polyamide residue with a mild ammonia solution.

6. Rinse off the excess mild ammonia solution at an ambient temperature.

7. Place the article in a hypophosphite based electroless nickel bath containing 1.5% ammonium bifluoride at about 190 to 200° F.

8. Rinse the article in mineral-free water at an ambient temperature, then dry and bake at 450°F for an hour.

---

[1] Bibber, J. W. 2013. Sanchem, Inc., U.S. patent US8388826B2.

Plating Titanium and its Alloys

Titanium is the ninth most abundant element in the earth's crust, but it is very difficult to prepare in its pure form as it reacts with carbon, nitrogen, oxygen, and silicon, all of which are associated with titanium ores. Initially, there was little need for having the element in its pure form as it was added to steel in amounts as small as 0.1% to prevent the formation of tiny pockets of small gas holes and to increase its tenacity and elasticity. The initial extraction methods heated the titanium ore with calcium metal, calcium hydride, or aluminum metal. If you used calcium or calcium hydride, then you would end up with titanium and calcium oxide, which could be dissolved with hydrochloric acid to give a fairly pure product. If you used aluminum, then you would get an alloy of titanium with a small percentage of aluminum; this was also used to improve the steel's properties and prevent the formation of gas holes in cast steel products. Another reason for the initial lack of interest in pure titanium is that over 90% of it is still used in the paint industry to make white paint, which is non-toxic and has exceptional sticking power.

The interest in producing pure metals began in the early 1950s with the advent of jet aircraft and various aerospace applications. Although pure metal is actually somewhat soft and elastic, it has a density of only 4.5, a melting point of about 1668° C. and, by itself, a tensile strength of about 63,000 pounds per square inch; this is as strong as many steels and twice as strong as the commonly used structural aluminum "6061". To obtain this, you need to heat titanium ore with carbon, which will leave an impure titanium. This is then heated to about 900° C. in the presence of chlorine gas to create titanium tetrachloride, which is then heated with sodium metal to give sodium chloride and pure titanium metal.

Almost all of the titanium is used to generate aluminum-titanium or aluminum-titanium-vanadium alloys for use in aerospace applications. One of the most commonly used and difficult to plate alloys is the 6% vanadium, 4% aluminum alloy. Titanium has an oxidation reduction potential (relative to a standard hydrogen electrode) of about -1.6 volts. The aluminum and vanadium only contribute to the generation of a tightly adhered oxide film that quickly reforms when exposed to the atmosphere. This is the primary reason as to why the alloy is so corrosion resistant and difficult to plate. In point of fact, only a handful of plating facilities are able to plate titanium and, as in the case of magnesium, there are a large number of rejects.

Conventional Electroless Nickel Plating on Titanium

An electroless nickel process, shown below, and used commercially may be found in: "Electroless Nickel Plating", Wolfgang Riedel, ASM International, www.asm-intl.org.

1. Degrease, if necessary.

2. Media blast the article with 220 mesh aluminum oxide at about 60 pounds per square inch.

3. Rinse in mineral free water.

4. Etch in a bath of 400 grams of concentrated nitric acid which contains 5.0 grams per liter hydrogen fluoride at an ambient temperature (titanium fluorides are insoluble in water).

5. Rinse in mineral free water.

6. Activate with an electrolytic nickel strike.

7. Rinse in mineral free water.

8. Use an "Electroless Nickel" bath.

9. Bake at 750° F. for 30 to 60 minutes.

Organic Electroless Nickel Process[1]

1. Degrease, if necessary.

2. Make the article the cathode in an electrochemical cell of 5% potassium hydroxide in water and a stainless-steel anode for about 30 seconds at an ambient temperature.

3. Rinse in mineral free water at an ambient temperature.

4. 30 second dip in a bath of 20% nitric acid and 1.5% ammonium bifluoride at an ambient temperature.

---

[1] Bibber, J. W. 2013. Sanchem, Inc., U.S. patent US8388826B2.

5. Rinse in mineral free water at an ambient temperature.

6. Etch the article for about 60 seconds in a bath of 20% sulfuric acid and 1.5% ammonium bifluoride at an ambient temperature.

7. Rinse in mineral-free water at an ambient temperature.

8. Make the article the cathode in an electrochemical cell of 5% potassium hydroxide and a stainless-steel anode for about 15 seconds at an ambient temperature. Reverse the polarity (about 7 volts) and make the article the anode for about 10 seconds to generate a light-yellow titanium oxide.

9. Rinse the article in mineral-free water at an ambient temperature.

10. Make the article the anode in an electrochemical cell consisting of a stainless-steel cathode and a dispersion of various polyamine acids and polyamides at an ambient temperature for about 2 seconds.

11. Rinse off the excess polyamine acids and polyamides with a mild ammonia solution at an ambient temperature.

12. Rinse off the excess ammonia at an ambient temperature.

13. Place the article in a 20% nitric acid and 1.5% ammonium bifluoride bath for about 15 seconds to remove the yellow titanium oxides. The polyamino acids and polyamides remain bonded to the article. Use an ambient temperature.

14. Dip the article in a 20% copper sulfate solution containing 5 grams per liter sulfuric acid and 1.5% ammonium bifluoride for about 15 minutes to give a uniform and even deposit of copper under the polyamino acid and polyamide film. Use an ambient temperature.

15. Rinse the copper sulfate solution off with mineral free water at an ambient temperature.

16. Place the article in the hypophosphite “Electroless Nickel" bath at about 95°C.

17. Remove the article, rinse with mineral-free water, dry, and bake at 450°F for an hour. The polyamine acids and polyamides remain in the nickel bath.

At this point you may plate just about anything you want over the nickel/phosphorous deposit using conventional methods.

Plating Molybdenum and Tungsten

The chemistry of the heavy elements is different because light metals only have a few bonding sites, while the large heavy elements may reach out and find many bonding opportunities on adjacent atoms. As a result, metals, such as tungsten and molybdenum, are quite strong and hard elements. Molybdenum and tungsten are considered together because both of them are used in the same industrial applications and have many of the same chemical and physical properties. Both elements are used to generate high strength steel. Molybdenum has a tensile strength of about 47,000 psi while tungsten has the highest tensile strength of all metals at 500,000 psi. Tungsten has the highest melting point of all metals at 3410° C., while molybdenum comes in at 2623° C. Diamond has a mohs hardness index of 10, while tungsten has a mohs hardness of 7.5 - 8.0 and molybdenum comes in with a figure of 5.5. Both elements are quite dense, with tungsten having a density of 19.3 grams per cubic cm. and molybdenum 10.22 grams per cubic cm. Both elements are rare, as they are heavy and sink down in the earth's crust.

The oxidation reduction potential of both elements is about + 0.2 volts relative to a standard hydrogen electrode and as such they are not very chemically reactive, as well as inert to most strong acids and/or bases. However, they will slowly react with strong nitric acid to generate tungstic oxide (tungsten bonded to three oxygen atoms) and strong alkalis will form tungstates (tungsten with 4 oxygen atoms attached). The chemistry of molybdenum is essentially the same.

Molybdenum ores consist of molybdenum sulfide or the lead salt of molybdate (molybdenum attached to four oxygen atoms). The sulfide is roasted in a furnace at high temperatures to create molybdenum trioxide and sulfur oxides may be converted into sulfuric acid. The molybdenum trioxide is then heated with carbon in an electric furnace with iron to give an iron alloy of molybdenum, which is added directly to various steels. Lead molybdate may be cooked with nitric acid to remove the lead in the form of lead nitrate. To get pure molybdenum, you must treat the crude oxides from either process with ammonia to get ammonium molybdate; this is purified by recrystallization and then heated to drive off the ammonia and leave the pure oxide behind. Reduction of the oxide with hydrogen gives a pure metal in the form of a very fine powder. Due to its extremely high melting point, the powder is put under about 7,000 pounds per square inch pressure and then heated to over 1000° C. This produces a hard crystalline mass. To make it possible to work with molybdenum, it needs to undergo vigorous beating or "swaging" as this decreases the size of the molybdenum crystals, which gives a ductile and malleable product. The molybdenum may now be drawn into wire or rolled into sheets. The same process takes place with tungsten ores and its resulting tungsten metal.

Plating Processes

In the case of the light metals, they are chemically reactive but were covered with a thin layer of metal oxides to give them an inertness which makes it difficult for them to attach to other metals. To get around this, electrochemical cells were generated on their surface with elemental zinc or tin. In organic processes, polyamine acids or polyamides displaced the metal oxides and then the nickel further displaces them, as this will attach itself to the metal being plated. In this case, the metal is inert. These metals only have an oxidation reduction potential of about + 0.2 volts relative to a standard hydrogen electrode; therefore, zincate and/or "stannates" are not used.

Westinghouse has used large amounts of tungsten and/molybdenum for some time and, in 1948, they took out a patent.[1] This process has more or less remained the same since then. It is not that much different from the ASTM "Standard Practice for the Preparation of Tungsten and Tungsten Alloys for Electroplating" ASTM Standards, Philadelphia, PA. Standard B 482-85 or the ASTM "Standard Practice for the Preparation of Molybdenum and Molybdenum Alloys for Electroplating, ASTM Standards, Philadelphia, PA. standard B 629-77.

Simply preparing tungsten and its alloys for electrodeposition is quite involved and requires high concentrations of hydrofluoric acid and/or sodium and potassium hydroxide. Once prepared, the parts must be immediately plated and you may be required to use a platinum anode. You will need to give the parts a chromium strike, which is then followed by a nickel strike, before depositing the required metal. The chrome strike must be from a 250 gram per liter chromic acid bath at 60 to 72° C. using a high current density. The nickel strike will come after a 20% hydrofluoric acid activation process, which is followed by an immediate rinse and then the deposition of the desired metal. Molybdenum preparations for electroplating will require cathodic cleaning for 30 seconds at 60 to 75° C. in a very strong alkaline cleaner, as well as rinses throughout the process in warm mineral free water (50° C.). Following a rinse, the molybdenum is electropolished

---

[1] Cannizzaro, Joseph J. 1948. "Westinghouse Electric Corp." U.S. Patent, US2443651.

in 80% sulfuric acid for 20 to 30 seconds at a high density current. Following a second rinse, the part is given a dip in a 45 gram per liter sodium hydroxide solution at an ambient temperature. This is followed by another warm water rinse and the part is then dipped in 10% sulfuric acid solution at an ambient temperature, given another warm water rinse, and electroplated in a 250 gram per liter chromic acid bath for 1 to 5 minutes at a high density current. In some cases, it may be necessary to first make the part the anode in the chromic acid solution for a minute at about 2200 amps per square meter in order to insure good adhesion. In other words, it may be necessary to etch the part in order to obtain a good bond for the metal being deposited. Another warm water rinse and you should be ready for the required nickel strike. After the nickel strike, the part gets another warm water rinse and is immediately plated with the required metal. At this point you may have sufficient bond strength and, if not, then strip the part and start over again.

Electroless Nickel Processes

The following process comes from Mallory, G.O., Haydu, J.B., "Electroless Plating: Fundamentals and Applications", William Andrew, AESF, 1990.

The preparation for electroless deposition is not as difficult, but still presents a challenge. After taking the necessary steps to remove any mill scale and/or metal working fluids and related soils, soak the part in a 215 gram per liter solution of potassium ferrocyanide containing 75 grams per liter potassium hydroxide at an ambient temperature for about 1 minute. This is to be followed by a warm mineral free water rinse (50° C.). Then place the part in a 10% potassium hydroxide solution at boiling point for 10 minutes followed by a warm water rinse. Immediately place the part in a 10% hydrochloric acid solution for 30 seconds at an ambient temperature; followed by another warm water rinse. Immediately activate the part palladium chloride (0.1 to 0.5 grams per liter) dip for about 10 seconds followed by another warm water rinse. Go into your electroless deposition bath immediately. When finished, give the part another warm water rinse. If desired, you may replace the palladium activation step with a “Woods Nickel” strike.

Organic Based Process

Ever since the issuance of a patent to “Westinghouse Electric, Corp” in 1948, essentially all processes for the deposition of metal on tungsten, molybdenum, and their related alloys have been centered around this basic process, as well as the use of strong acids in the preparation of metals for deposition. Acid conditions are excellent for the generation of high molecular mass, but find it difficult to remove oxides of tungsten, molybdenum, and their related alloys. Strongly alkaline conditions generate little more than the corresponding molybdate and/or tungstate plus six oxides, which are reasonably soluble in water and easily removed under alkaline conditions. As a consequence, this process is operated almost entirely under alkaline conditions. The parts are cleaned of any mill scale and/or metal working fluids and related soils, which may or may not involve the use of mild acid cleaners. The clean parts are then made in the cathode of an electrochemical cell, which consists of 5% potassium hydroxide and a stainless steel or otherwise inert anode at an ambient temperature for about 30 seconds. The parts are then rinsed in mildly alkaline mineral-free water at an ambient temperature and immediately placed in an electrochemical cell, which consists of an alkaline dispersion of various polyamines and polyamides at an ambient temperature for 2 to 3 seconds. A mildly alkaline ammonia water solution is then used to rinse off any excess polyamines or polyamides. This process effectively displaces essentially all oxides from the surface of the parts being processed and effectively prevents the formation of any unwanted oxides on. The parts then go into an acid copper sulphate solution for about two minutes in order to generate a very thin and uniform layer of copper, while leaving most of the polymeric film in place to prevent oxide formation. The parts are then rinsed with mineral free water at an ambient temperature and placed in a strong alkaline hypophosphate electroless nickel bath at an ambient temperature. In about one hour, the polymers are displaced out into the bath and the parts will have a 0.0005 to 0.001 cm film of electroless nickel. At this point, the parts may, if so desired, be electroplated with acid or alkaline copper followed by the deposition of other metals, if necessary. Repeated testing has shown that the bonds of molybdenum and/or tungsten on the deposited metals are quite strong and pass all standard adhesion tests.

BIBLIOGRAPHY

Spadafora, S.J. 1992. "Naval Air Warfare Center Aircraft Division Warminster", Pa., Report No. NADC-92077-60

Spring, S. Industrial Cleaning. 1974. Prism Press, Melbourne, AU

Warmant, G. and Tartinville, J. 1954. Brit. Pat. 815,756

Elliott, jr. R.H. 1959. Pennsalt Chemicals Corp., US Pat. 2,918,357

Elliott, jr. R.H. 1959. Pennsalt Chemicals Corp., US Pat. 2,882,135

Ihsan K. Al Naimi, Moneer H. Al Saadi, Kasim M. Daws & Niels Bay. 2015. Influence of surface pretreatment in resistance spot welding of aluminum AA1050, Production & Manufacturing Research, 3:1, 185-200, DOI: 10.1080/21693277.2015.1030795

U.S. patent: 5304257

U.S. patent 3,171,765

F. Altmayer. 2004. "Testing Finished Parts for Hex Chrome", Plating and Surface Finishing, 91 (12), 20.

Bauer, O. and Vogel, O. 1923. German Patent 423,758

Acta Bioeng Biomech. 2017; 19(2):65-72

Thompson, J.S. 1943. U.S. patent 2,234,206 and 2,312,855; and patent 1,007,069

Darsey, V.M. and Cavanagh, W.R. 1946. Electrochem. Soc. Preprint 91-1

Anchem Products, Inc. 1971. Brit. Pat. 1,324,460

Danilidis, I. et. al., "Manganese-Based Conversion Treatment", University of Oxford, Oxford, U.K.

Spadafora, S.J. 1992. "Naval Air Warfare Center Aircraft Division Warminster", Pa.

Bibber, J. 1999. Corrosion 99, paper #491, NACE International, Houston

Brinker C.J., and C. Scerer. 1990. "Sol Science," Academic Press, New York

Filliagi, M.J. et al., J. Biomed Mat., 33:225; 1996

U.S. patent, US4191596

Lindert, A. and J.I. Maurer. "New Polymeric Materials for Metal Conversion Coating Applications", ACS Symposium Series, ISSN 0097-6156, 322 p. 209

Carson, L.R. 1993. "Third Annual Workshop on Chromate Replacements in Light Metal Finishing", Albuquerque, N.M.; Sept. 15-16, 1993

Bernard, W.J., Randall J.J., jr. 1960. Journal Electrochem. Soc.,107,483.

Diggle, John W., Vijh, Ashok, K. 1976. "Oxides and Oxide Films", volume four, Marcel Dekker, pages 214 217.

S. Wernick, R. Pinner and P.G. Sheasby. 1987. "The Surface Treatment and Finishing of Aluminum and its Alloys", Finishing Publications LTD,page 222.

Bibber, J., U.S. patent, US4988396A

Levin, M. L. 1957. "Trans. Farday Soc., 1958, 54, 935-940" Dept. of Chemical Engineering, Imperial College, London, S.W.7, November 11, 1957.

Pittman, Richard D. 1963. Northrop Grumman Guidance and Electronics Co., Inc. U.S. patent US3375179A

Diggle, John W. 1976. Vijh, Ashok, K. "Oxides and Oxide Films", volume four, Marcel Dekker, pages 203 -219

S. Wernick, R. Pinner and P.G. Sheasby. 1987. "The Surface Treatment and Finishing of Aluminum and its Alloys", Finishing Publications LTD. Page 778.

Diggle, John W., Vijh, Ashok, K. 1976. "Oxides and Oxide Films", volume four, Marcel Dekker, pages 203 -211.

S. Wernick, R. Pinner and P.G. Sheasby. 1987. "The Surface Treatment and Finishing of Aluminum and its Alloys", Finishing Publications LTD., page 799 – 800.

Berman, Elizabeth, Mason, Robert B. 2017. "Reducing Chromium plus six in Military Anodizing Operations", Products Finishing, volume 81/No.5, February 2017, pages 17-19.

Dunham, R.S. 1931. British Patent 393,996.

Venables, J.D., McNamara, D.K., Chen, J.M., Sun, T.S. and Sun, T.S. and Hopping, R.I. 1979. Applications of Surface Science, 3, 88-98.

Yukimori Moji, J. Authur Marceau, Boeing Co., U.S. Patent: US3959091A

Theodore M. Pochily Worthington E. Parker, U.S. Patent: US3338805A

https://doi.org/10.1002/bbpc.19580620615

https://www.atsdr.cdc.gov/ToxProfiles/tp58-c3.pdf

Danilidis, I., 1998. et. al., "Manganese - based Conversion Treatment," Dept. of Materials, University of Oxford, U.K.

Biestek, T. and J. Weber. 1976. "Electronic and Chemical Conversion Coatings", p. 74, Portcullis Press Ltd., Redhill, Surrey, U.K.

United States patent Application, US20150050518A1

D.W. Shoesmith, S. Sunder, M.G. Bailey, G.J. Wallace, F.W. Stanchell, "Anodic Oxidation of Copper in Alkaline Solutions: Part IV. Nature of the passivating film," Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 143, issues 1-2, 1/10/83, P. 153-165.

Keil, A., Metalloberflache. 1957. 11,44.

Wallbank, A.W.,J. 1952. Electrodepositors Technical Soc. 28, 209

Edwards, J. and Swanson, C. J. 1953. "Trans. Institute Metal Finishing". 29, 209.

Hewitson, E. H. 1927. (Eastman Kodak), U.S. Patent 1,627,900.

Petrocelli, J.V. 1950. "J. Electrochem. Soc.," 97, 10; 1951, 98, 183; 1952, 99, 513.

Brown, M., Schulburg, V. and Dell, G. 1936. Automotive Ind., 75, 884.

Krammer, O. 1945. "Metal Industry", 66,121.

Zimmerman, J. 1967. (Sperry Rand Corp.) U.S. patent 3,340,164.

Travers, W.J. 1931. U.S. Patent 1,971,761.

Mallory, G.O. 1985. "Plating and Surface Finishing", 72, No. 6, 86.).

Brenner, A. and Riddell, G.E.J. 1946."J. Research Nat. Bur. Stand. 37, 1-4.

Mallory, G.O., J.B. Hajdu. 2009. "Electroless Plating: Fundamentals and Applications", A.E.S.F. p. 72-74.

Bibber, J.W. 2013. Sanchem, Inc., U.S. patent US8388826B2.

Dow Chemical Company. U.S.A. 1982. Inorganic Chemicals Dept. *Operations in Magnesium Finishing.*

Cannizzaro, Joseph J. 1948. "Westinghouse Electric Corp." U.S. Patent, US2443651.

INDEX