Conversion Coatings

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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.

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[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

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[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

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[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.