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SESSION L

AMERICAN ELECTROPLATERS' SOCIETY, INC.

70TH ANNUAL TECHNICAL CONFERENCE - INDIANAPOLIS, IN

LIGHT METAL FINISHING II

SESSION L

Light Metal Finishing II
Session L

Alkaline Corrosion of Anodized Aluminum: Cause and Cure

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ALKALINE CORROSION OF ANODIZED ALUMINUM: CAUSE AND CURE

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FMC Corporation is a large supplier of detergent components to formulator-compounders of various types of cleaners. In an investigation of the effect of carwash detergents on painted surfaces and automotive aluminum trim, we found that some carwash products caused discoloration of bright anodized aluminum trim parts. Representatives of car manufacturers, aluminum producers, aluminum fabricators and suppliers of carwash detergents were aware of the problem. The phenomenon was commonly called aluminum "blush" or aluminum "buttermilking". The discoloration shows up as an unsightly white film and, once formed, it cannot be removed. We decided to investigate the problem further when we learned that the mechanism of attack was not fully understood and that there were no guidelines for preventing its occurrence.

An aluminum producer defined blush as "the partial dissolving of the amphoteric anodic coating by acid materials below pH 4 and alkaline materials above pH 10". Note that the anodic coating, not the aluminum metal is dissolved. In our research, we found this description approximately fits one of the three types of anodized aluminum corrosion we observed. We called it alkaline attack. The other two types are sodium chloride blush and chelate related blush. The concept of chelate related blush is new and unexpected. Each type of corrosive attack is different in appearance and will be described more fully.

Figure 1 provides an estimate of the growth in the use of aluminum in, and on, cars. Currently an average of over 125 pounds of aluminum per car is used and projections are that this will more than double during the 1980's. Weight reduction to improve fuel efficiency is an important strategy of car makers in order to meet government requirements on their fleet average. Aluminum and other light weight materials are being used for both internal and external applications.

This paper deals with the external use of bright-anodized aluminum trim and components such as side body mouldings, window trim, mirror frames, wheel covers and bumpers. However, we believe that the type of corrosion under discussion applies to all applications where anodized aluminum is contacted by alkaline cleaners such as appliance trim, patio furniture, and handrails etc. in commercial buildings.

When these anodized aluminum pieces are processed by an aluminum finisher, the porous anodic film is sealed in a manner that protects it and the substrate aluminum from penetration by moisture and other sources of corrosion. In the case of bright dipped and anodized aluminum, the mirror like finish will be protected for many years when the sealing step is effectively done. Our work involves the use of bright anodized aluminum sealed in a hot water bath containing small quantities of nickel acetate. We believe that nickel ions enter the open pores in the hexagonal cells and attach to other metal ions that form the anodic film structure and that the anodic film (aluminum oxide) is converted to aluminum hydrate thus swelling and closing off the pore openings. Figure 2 shows the idealized structure of the cells and pores of the anodic film.

To deal with the aluminum blush problem we developed a small lab scale test to evaluate what components or characteristics of alkaline cleaners would cause blush. Figure 3 shows our test apparatus which consists of a constant temperature bath with a test tube containing a piece of anodized aluminum trim immersed in a test solution. In this static immersion test method, at a temperature of 120°F, blush would develop in four hours (or less) with some commercial carwash detergents (used at 0.25%) or not at all with other products regardless of the length of time the aluminum sample remained immersed. The aluminum samples used in these tests were obtained from job shop anodizers and represented 5XXX series trim alloy and 7XXX series bumper alloy. The carwash detergents were also commercially used products.

We found three distinctly different types of anodized aluminum blush. The first, "Alkaline Attack" attacks and dissolves the anodic film when the solution pH is greater than 10. In this form of corrosion, hydroxyl ions in the test solution penetrate the protective film and roughen the underlying aluminum metal surface. A dense white discoloration develops. We also observed that a typical aluminum hydroxide precipitate formed in the test solution. With further tests we determined that this type of corrosion can be prevented by inhibiting the active alkalinity of the cleaning product through the addition of a specific quantity of silica to the product.

When the cleaning product contains a silica (SiO_2) to active alkalinity (Na_2O) ratio of 0.8 or greater, we found that alkaline attack would not occur even at a pH of 12.3. We have recommended an SiO_2/Na_2O ratio of 1.0 to formulators of detergent which contact anodized aluminum trim.

The second type of aluminum blush found was termed sodium chloride corrosion. This occurs when sodium chloride is used as an inexpensive filler in detergents. In this case the oxide film is also dissolved but in more localized areas and clusters of pits can be seen in the aluminum metal. Some white discoloration is also seen. We were unable to develop a procedure for preventing this type of corrosion except to advise compounders to avoid the use of sodium chloride in detergents which will be used on anodized aluminum.

The third type of blush corrosion was called chelate related blush. Chelating chemicals such as complex phosphates are an essential ingredient in cleaning compounds. Their purpose is to build or support the cleaning efficiency of the surfactant through sequestration (or chelation) of water hardness ions. Components of the detergent with metal ion complexing capabilities function by re-opening the sealed pores in the oxide film and complexing, or chelating, the nickel used in the sealing process. A white deposit is formed and spreads laterally across the barrier layer of the pores. The anodic film isn't completely penetrated so there is no corrosive attack of the underlying aluminum metal. We used our scanning electron microscope and elemental mapping for nickel to determine the mechanism involved in this type of attack.

With organic chelators present in the test solution, we noted a significant decrease in nickel ion concentration in, and on, the anodic film surface where blush occurred. On non-blushed test specimens, the elemental nickel mapping showed little or no change in the pattern or occurrence of nickel in the anodic film.

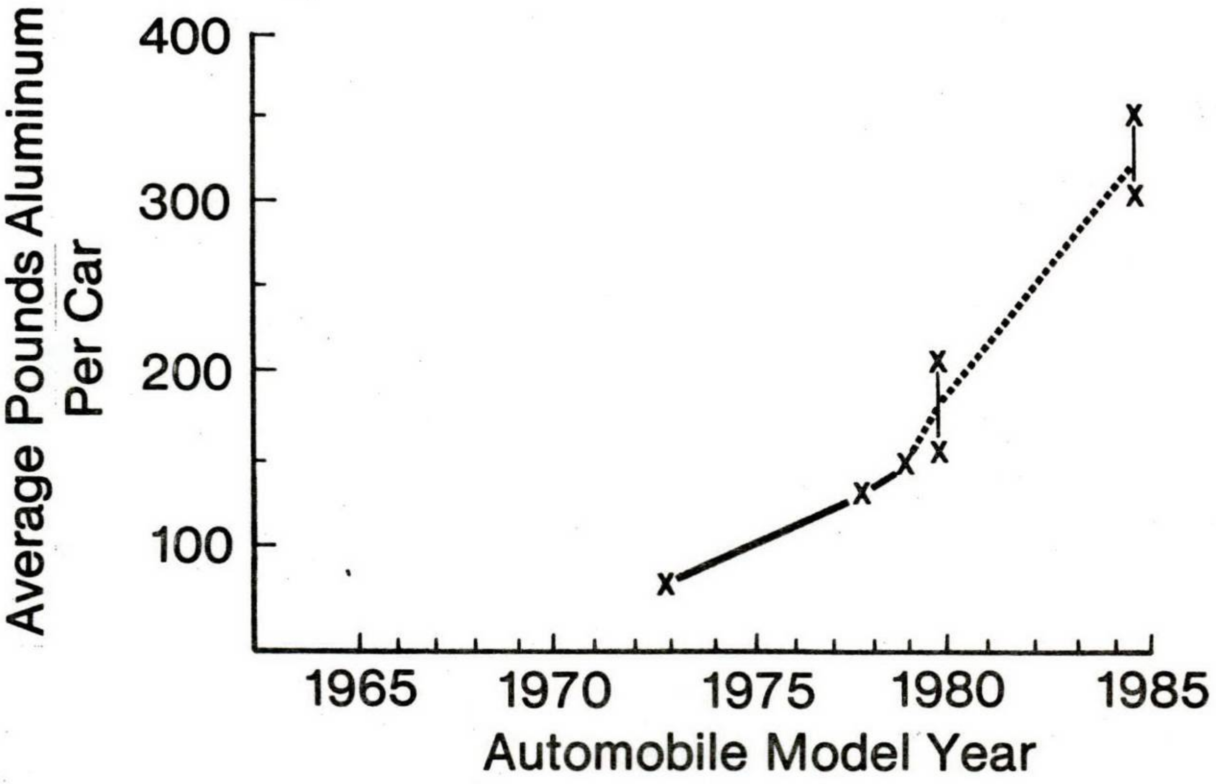
The time required to develop a blushed condition was dependent on the aluminum alloy being used and the binding strength of the chelator present in the detergent. Figure 5 shows the time it takes for various organic and inorganic chelators to produce chelate related blush. To avoid the potential for confusing two types of blush, these data were obtained in uninhibited test solutions having a pH of 9.8. The organic chelators re-open the pores and complex the nickel ions much faster than do the inorganic phosphates. They also attack the film in all areas whereas the phosphates only cause blush in areas where the anodic film's geometry has been distorted due to bending or otherwise stressing the metal surface. Figure 6 further illustrates these comments. The figure shows an end view of window trim and the areas where blush tends to occur, that is, it occurs on the bends and adjacent to places where the metal was cut. Blush doesn't occur on the inner surfaces of the trim piece even though the anodic film is less thick than the film on the outer surfaces. Our opinion is that this is due to compressive distortion of the film which helps the film resist penetration of corrosive materials. Figure 6 also has electron microscope views of chelate blushed and unblushed anodized surfaces. Scanning electron microscope scans for nickel revealed no nickel in or near these holes but nickel was found uniformly over the unblushed region of the anodic film. The figure points out blushed areas where fabrication has caused metal distortion and the attack is due to inorganic chelate related blush. When the stronger, organic, chelators come in contact with anodized aluminum, blush tends to occur on all areas, not just those where the anodic film has been distorted.

This type of blush is prevented through the use of a silica inhibitor added in certain definite proportions to the chelator contained in the alkaline cleaning product. The 7XXX, zinc containing bumper, alloy is more reactive than the 5XXX, magnesium containing, alloy so more silica inhibitor is required. When the organic chelators such as NTA, EDTA or citrates are present in the cleaning product, about four times as much silica inhibitor is needed than is required when the chelate is an inorganic phosphate. The minimum effective level of inhibition for 5XXX series alloys is 20 parts of silica per 1000 parts of inorganic phosphate; the highest level needed is 160 parts of silica per 1000 parts of organic chelator. Further tests showed that these inhibitor use levels completely eliminated chelate related blush.

In this study we have provided an explanation of the mechanisms which lead to three types of blush corrosion of anodized aluminum. A simple laboratory test method was developed which reliably predicts blush tendency. The capability of the electron microscope for examining surface defects and developing information on the causes of those defects was demonstrated. The understanding of blush corrosion and how to avoid its occurence was significantly advanced.

Hopefully dissemination of this knowledge will lead to increased use of bright-anodized aluminum.

Figure 1.
Automotive Aluminum Usage



Sources: Aluminum Association, 1977 Aluminum Statistical Review
Aluminum Association, Use of Aluminum in Automobiles—Effect on the Energy Dilemma, Publication T12

Figure 2.
Anodizing

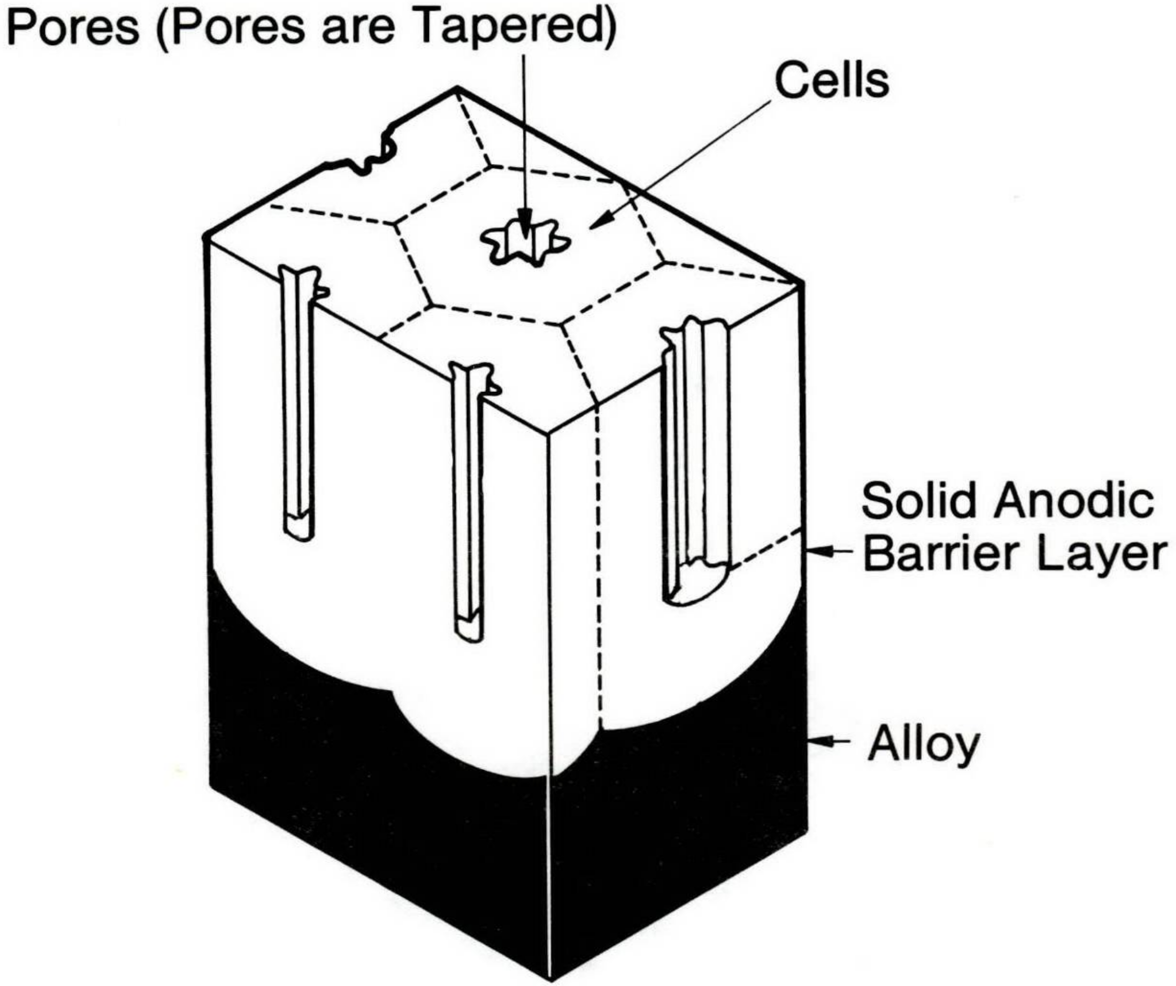


**Figure 3.
Blush Test Apparatus**

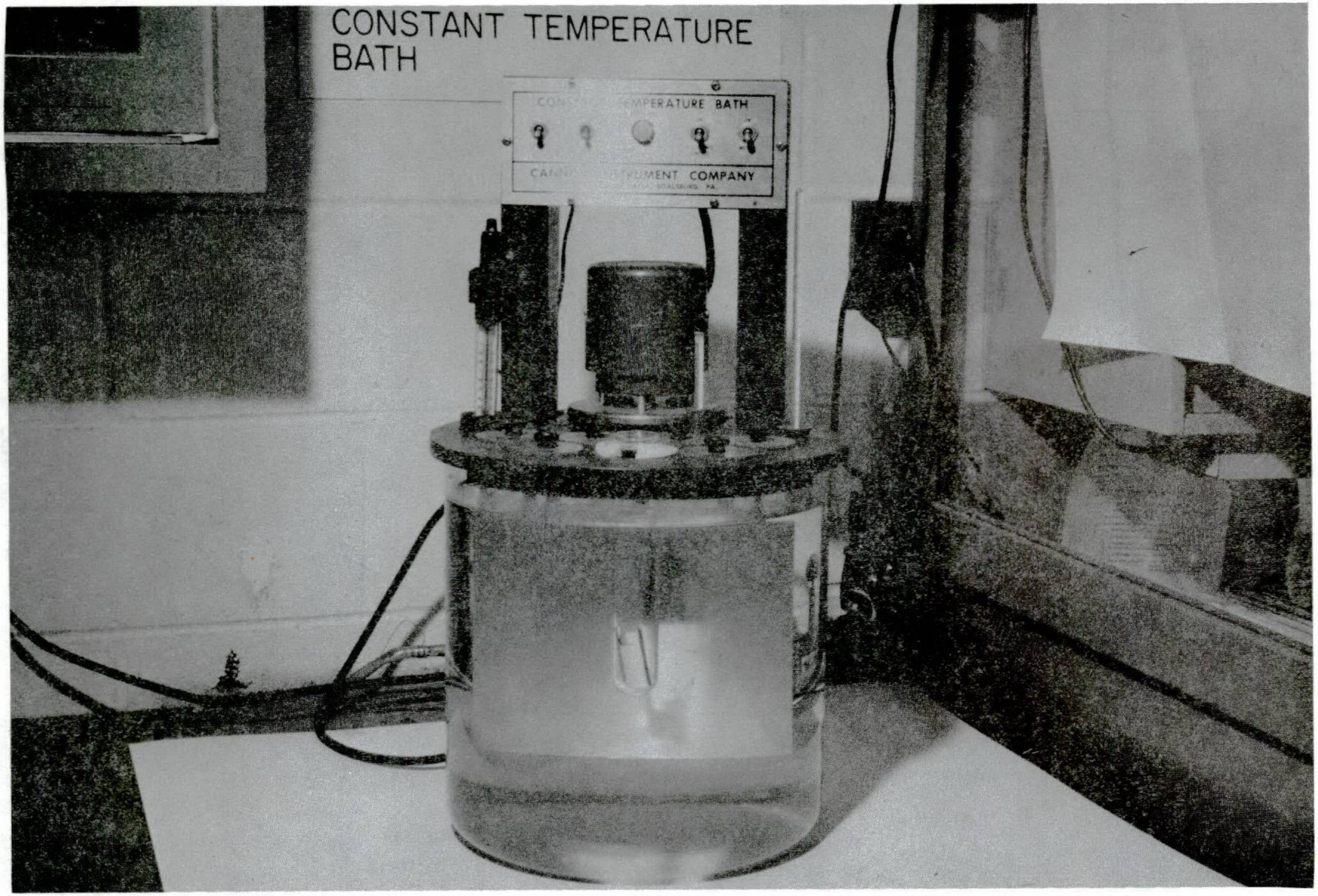


Figure 4.
FMC Studies
Have Identified Three Types of Attack on the Anodic Coating

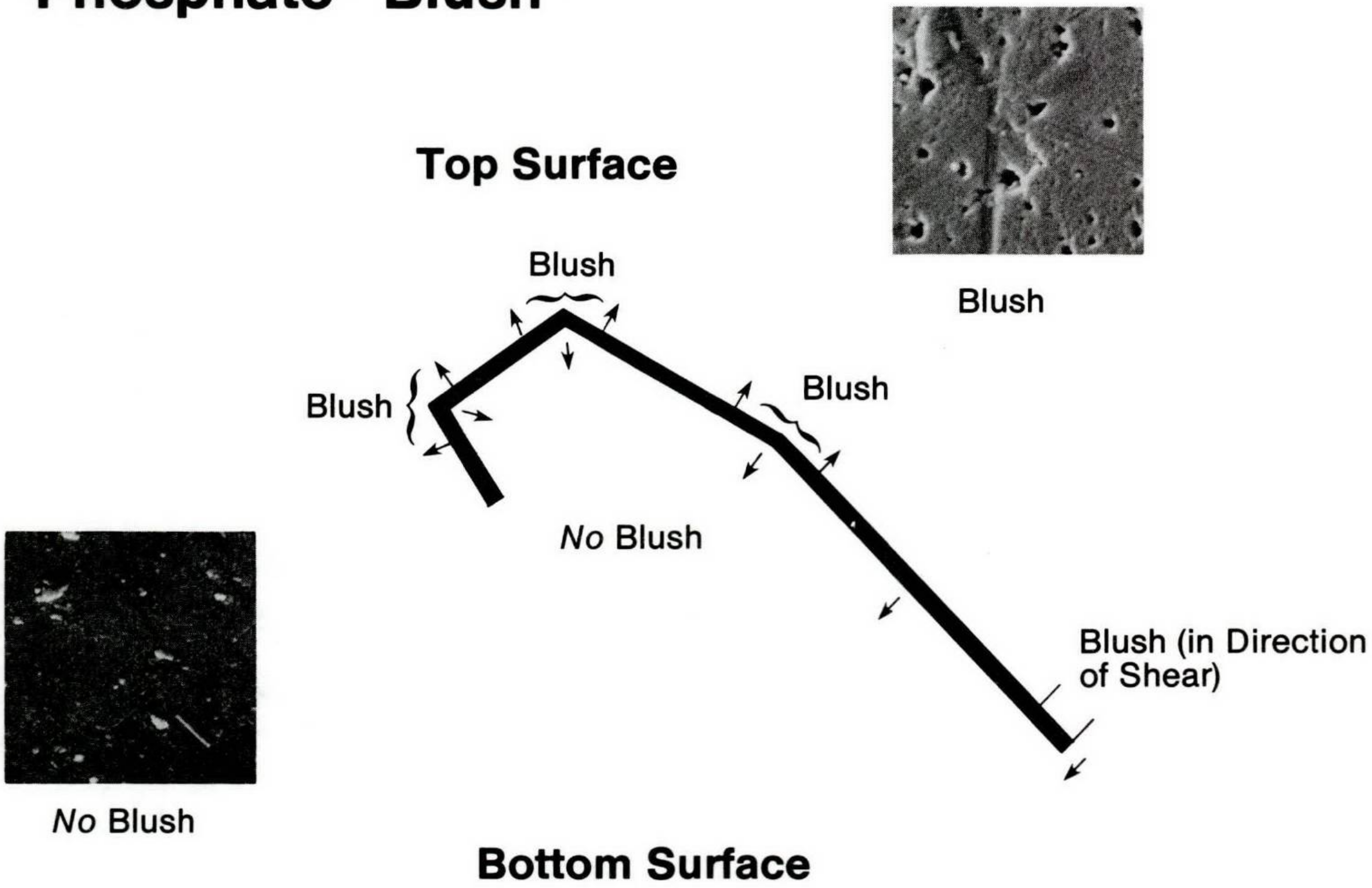
- ALKALINE ATTACK
- SODIUM CHLORIDE CORROSION
- CHELATE RELATED BLUSH

Figure 5.
Rate of Chelate Attack on Anodized Aluminum Automobile Trim (5252 Alloy)

Chelate	Time to First Visible Blush, min[1]	Site of Attack
EDTA	7	All Surfaces
NTA	13	All Surfaces
Citrate	35	All Surfaces
TSPP	42	Stress Sites
STPP	70	Stress Sites
Glassy Phosphate	80	Stress Sites

[1] Test Conditions:
0.25% Solution
150 ppm Water
pH 9.8
Temp. 120°F

**Figure 6.
End View of Trim-piece Showing Sites of Poly-Phosphate "Blush"**



L-2

Light Metal Finishing II
Session L

How to Prevent Pitting on Color Anodized Parts when Using Titanium Anodizing Racks

Fred Henschel
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HOW TO PREVENT PITTING ON COLOR ANODIZED PARTS WHEN USING TITANIUM ANODIZING RACKS

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Many anodizers do not use titanium racks because they have encountered pitting on dyed parts and some on clear parts. On clear parts the pitting only appears after sealing. It is only natural for anyone to find the simplest, quickest and most expedient solution to a problem which, in this instance, is to use aluminum racks. Yes, aluminum racks add to the contamination of the anodizing bath...

Yes, aluminum racks must be stripped every trip through the line.

Yes, aluminum racks are quickly consumed and must continually be replaced. However, this solution precludes all of the cost-saving advantages of Titanium racks.

The purpose of this discussion is to show you that pitting problems in color anodizing are completely controllable without any costly, specialized equipment or changes in your regular procedure. And, you can use Titanium racks to full advantage.

A Lesson Learned At Sea

Unfortunately nobody has bothered to inform the anodizer that the pitting he is experiencing is caused by "galvanic action" or "galvanic corrosion," an extirely controllable problem. Mariners have had to deal with the problem for over a hundred years when utilizing more than one metal below the waterline of boats and ships. For example, a steel-hulled ship with bronze propeller. Thus, to learn something about this phenomenon let's begin by looking at the definition of galvanic corrosion as stated by the Boating Technical Standard's Body of the American Boat and Yacht Council.

Galvanic corrosion is "the corrosion that occurs at the anode of a galvanic couple, caused by the flow of ions from the anode to the cathode through an electrolyte." Another way of stating it would be that two dissimilar metals, submerged in a liquid which will easily carry a current, can cause the eating away of one of the metals.

Which one? The galvanic table (Figure 1) shows us.

At the top of the list are the most active metals or the most anodic. At the bottom, the least active, or most cathodic. Note that maganesium heads the list followed by zinc and aluminum, whereas titanium is only surpassed as a noble metal by graphite, zirconium, gold and platinum. In galvanic corrosion, the more active metals will become corroded in the presence of a lesser active metal.

Electrolytes Are The Key

Sea water is an excellent electrolyte. Tap water is generally not. However, when tap water contains a great many minerals and particles it can become a fair electrolyte. The addition of chemicals can considerably enhance the electrolytic properties of tap water. Thus, virtually all of your tanks will have current carrying capacities to some degree. But, the only tanks in which parts are left for any length of time after anodizing are the dye tanks and the seal tanks. These are the ones which can cause the anodizer galvanic corrosion difficulity.

The American Boat and Yacht council also emphatically warns boaters that stray currents, especially from A.C. sources, can also play havoc with galvanically dissimilar metals in sea water (or in our case, in the dye or seal tanks). Stray currents can be present in your tanks, at unacceptabale levels, because of your rectifiers, many of which are located in the vicinity of these tanks. Also, electric immersion heaters, used in many shops for heating these tanks, can contribute to stray current conditions.

Do not underestimate the effect these currents have, for they can be the major factor in creating a galvanic corrosion problem.

The worst condition would have to be in a plastic or fiber glass tank, or in a metal tank lined with plastic or rubber because the electrolyte has no connection to ground as a result of the insulating effects of the tank or liner. Adding insult to injury, our worst case would have an old electric immersion heater, located in an area near a big rectifier, with 140^{o} black dye made with late summer tap water somewhere in Southern California. Believe it or not, we found just such conditions in a Van Nuys, California anodizing operation. Their rectifier is about 18 feet from their black dye tank. They have an old electric immersion heater in a plastic tank.

Here are some test coupons (Figure 2) which we anodized under these conditions, using a titanium rack. These samples are the first of a series we ran in February. They were in the dye tank about 18 minutes. Note the pitting problem.

Later in this report, we will show you other test coupons run through the same system after the galvanic corrosion problem had been eliminated. You will be truly amazed!

The Sacrifical Anode Solution

But first, back to the control of galvanic corrosion in marine applications. Let's see how the mariner's solution can be adapted to an anodizing plant situation.

First, many decades ago "in the olden days," as the younger generation says, zinc blocks were attached to the hulls of metal ships just forward of the screws and rudder. It was found that magnesium, the most active or least noble of all metals, would practically disappear before your eyes when submerged in sea water. So, zinc was the next choice. It lasted and performed well because it was more active or anodic than any of the ship's metals exposed under water and, thus, acted as a sacrificial anode. So long as the zinc was not completely comsumed it protected the most anodic metal of the ship itself. This method is still used today on small ships and boats.

Anodizers can do even better than mariners, for dyes and seals don't attack magnesium the way sea water does. So, with the best sacrificial anode in use, we can expect the best protection for our aluminum parts in those tanks which typically cause pitting problems.

The sacrificial anode is the first major step in solving your pitting problems. Before we discuss how to install your sacrificial anodes, you'll want to help yourself even more by first reducing any stray current problems which may exist.

Since you aren't about to move tanks or rectifiers, the next best way to eliminate stray current is to ground your tanks with a good copper wire, leading it to some ground other than water pipes, as that would just spread current to all the tanks. If your tank is plastic or rubber lined, drop the wire into the solution. Otherwise, bolt the wire to the tank. It's just that simple. No big expense or need to shut down your production. Ground your tanks to conduit or an electrical box.

Now, it is time to obtain magnesium anodes about the same length as the spline and hook of your longest titanium racks. Vulcanium Corporation supplies square bar anodes complete with hooks to any length required (Figure 3). Before putting these sacrificial anodes in your dye and seal tanks you must first deoxidize the magnesium to remove any oxide coating which might reduce efficiency. This can be done in any nitric acid-based de-oxidizer used in your anodizing line.

After anodizing and before dying and/or sealing, place your sacrificial anodes on the workbar, on either side of the titanium rack or racks being used. A clamp, wire or hook can be used to secure the anodes in place on the workbar. We recommend the use of clamps such as Vulcanium Corporation's Spartan Clamp as it is completely corrosion resistant. If your tank is big and your load consists of many racks, it may be necessary to use more than two sacrificial anodes to protect the centermost racks. Be sure to position the sacrificial anodes as close to your racks as is practical, for the closer to the parts, the more effective your galvanic protection.

Earlier we reviewed examples of test coupons from a worst-case situation involving galvanic corrosion. The samples were liberally pitted, the result of galvanic corrosion in the dye tank. Now, take a look at these (Figure 4) test coupons. The one on the right is from our original test. The one on the left was run on the same anodizing line, the same afternoon, using the same time intervals and the same Titanium anodizing rack. Note the smooth, flawless surface and exceptionally fine quality finish. The difference is truly amazing and due entirely to elimination of galvanic corrosion.

A good deal has been said over the years about the problems encountered when using Titanium anodizing racks, especially on color work. It is hoped that this explanation of controlling galvanic corrosion will encourage you to look at your own production line and adapt the concept of sacrificial anodes to it. Now, you can take advantage of long-lasting Titanium racks. You can do so with confidence. Your parts will turn out perfectly, for you will be protecting them from galvanic corrosion, easily and economically.

ELECTROMOTIVE OR
GALVANIC SERIES FOR METALS

+ Anodic
(least noble)
corroded

-Cathodic
(most noble)
protected

Magnesium
Magnesium alloys
Zink
Berillium
Aluminum 5052, 3004, 3003, 1100, 6053
Cadmium
Aluminum 2117, 2017, 2024
Mild steel (1018), wrought iron
Low alloy high strength steel, cast iron
Chrome iron (active)
430 Stainless (active)
302, 303, 321, 347, 410, 416, stainless steel (active)
Ni-resist
316, 317 stainless steel (active)
Carpenter 20Cb-3 stainless (active)
Aluminum bronze (CA 687)
Hastelloy C (active) Incbnnel 625 (active) Titanium (active)
Lead/Tin solder
Lead
Tin
Inconnel 600 (active)
Nickel (active)
60 Ni-15 Cr (active)
80 Ni-20 Cr (active)
Hastelloy B (active)
Naval brass (CA 464), Yellow brass (CA 268)
Red brass (CA 230), Admiralty brass (CA 443)
Copper (CA 102)
Manganese bronze (CA 675), Tin bronze (CA 903, 905)
410, 416 Stainless (passive) Phospher bronze (CA 521, 524)
Silicon bronze (CA 651, 655)
Nickel silver (CA 732, 735, 745, 752, 754, 757, 764, 770, 794
Cupro Ni 90-10
Cupro Ni 80-20
430 Stainless steel (passive)
Cupro Ni 70-30
Nickel aluminum bronze (CA 630, 632)
Monel 400, K500
Silver solder
Nickel (passive)
60 Ni 15 Cr (passive)
Inconnel 600 (passive)
80 Ni 20 Cr (passive)
Chrome iron (passive)
302, 303, 304, 321, 347 stainless stainless steel (passive)
316, 317 stainless steel (passive)
Carpenter 20 Cb-3 stainless (passive), Incoloy 825
Silver
Titanium (passive), Hastelloy C & C276 (passive), Inconnel 625 (passive)
Graphite
Zirconium
Gold
Platinum

Figure 1 - Galvanic Series Table
Table shows relative degrees of activeness of various metals. The higher on the list, the more active (susceptible to corrosion) the metal. Note the relative positions of aluminum (5th from top, 7th from top) and titanium (5th from bottom).

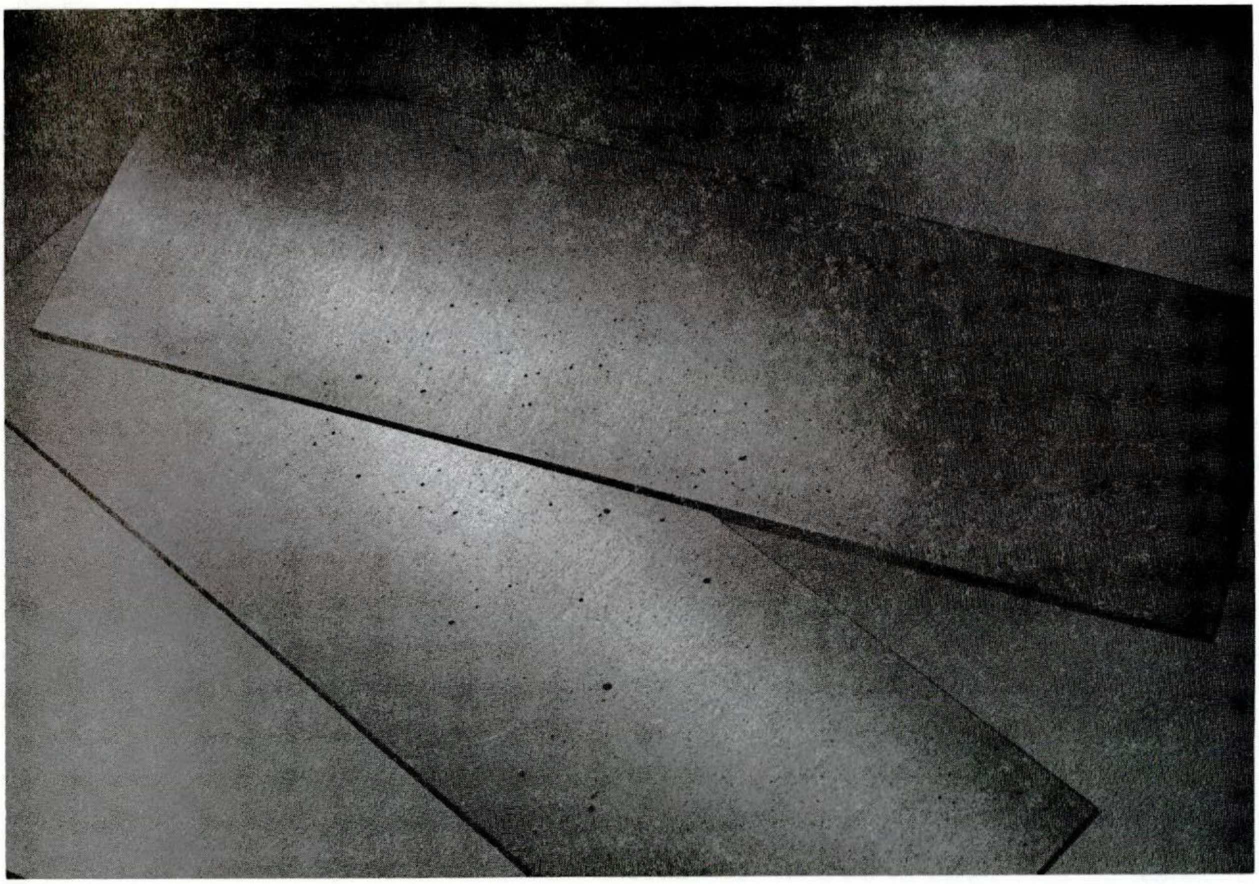

Figure 2 - Black anodized test coupons show the effects of galvanic corrosion. Pitting appears across surface.

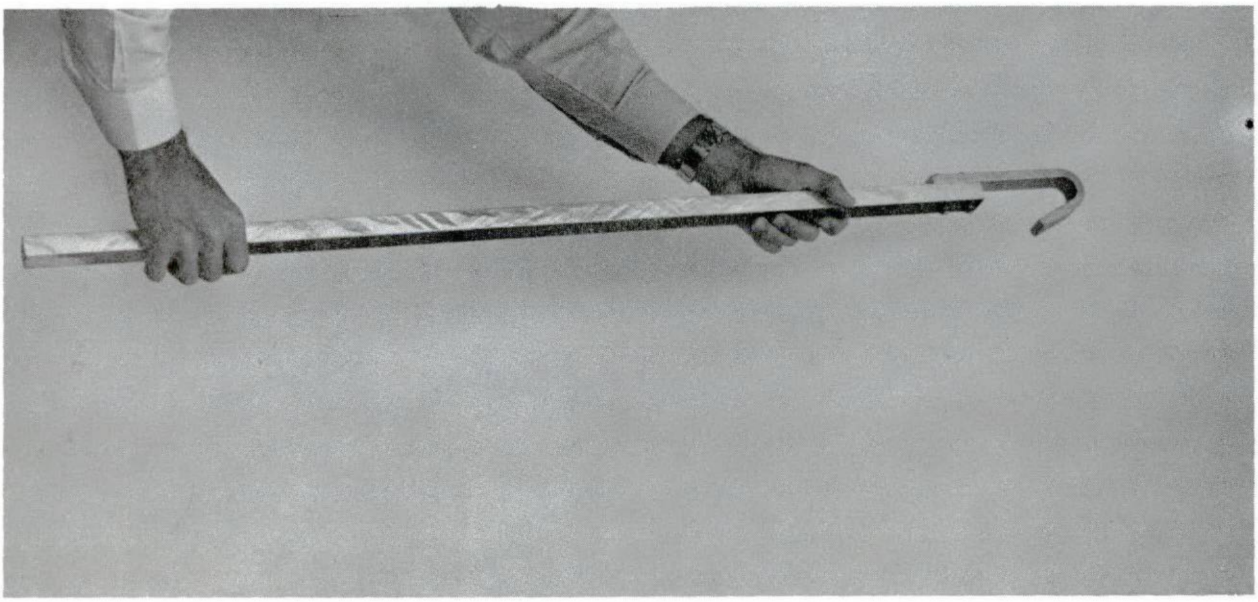

Figure 3 - Sacrificial magnesium anode is used to divert galvanic corrosion attack away from aluminum parts.

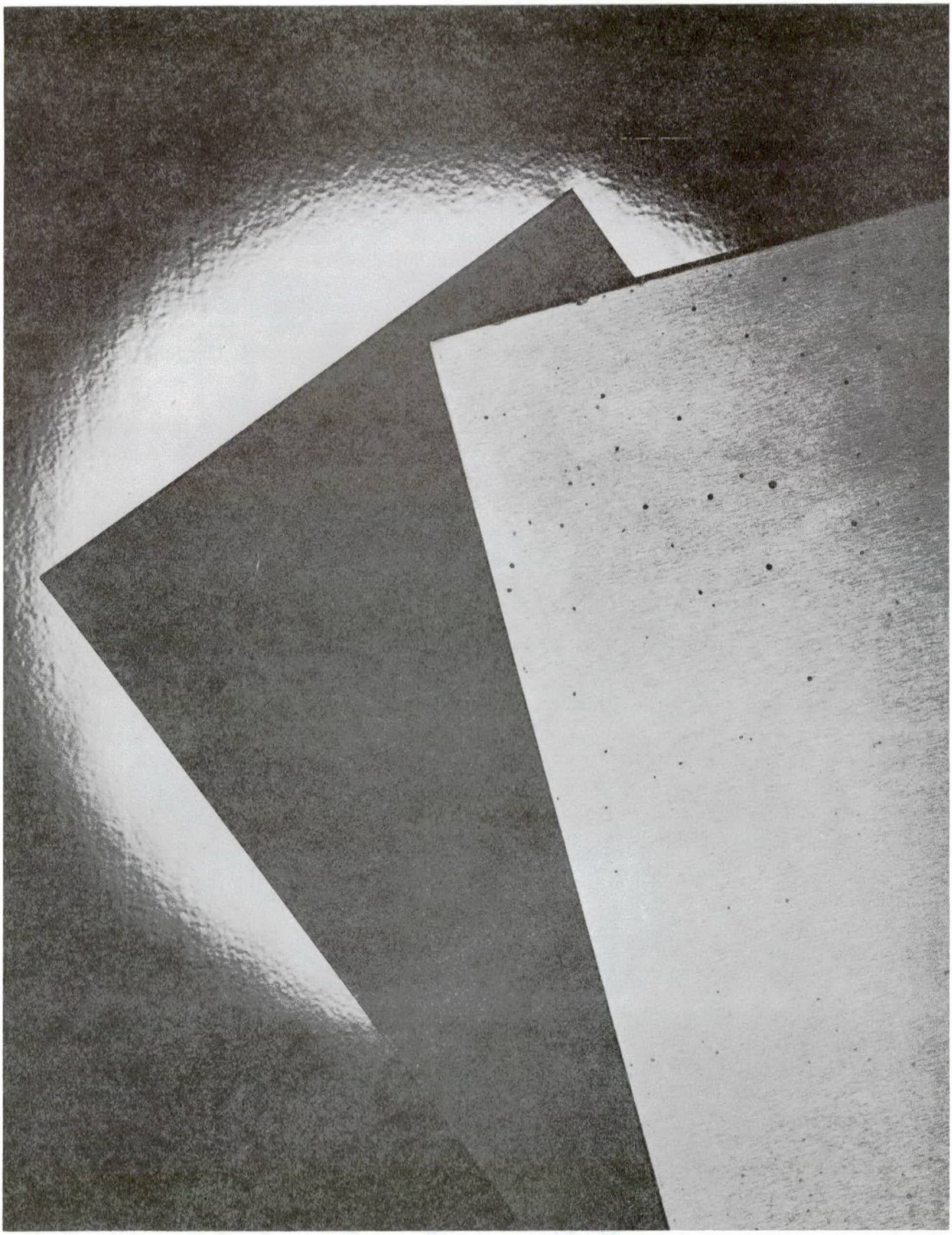

Figure 4 - Test coupon comparison shows pitted part (right) versus part anodized in the same system (left) with a sacrificial nagnesium anode used. Note: different "color" of coupons is due to photographic lighting technique needed to show pitting. Both coupons are black anodized.

L-3

Light Metal Finishing II
Session L

Chromate Conversion Coating Processes of the Conventional and Nonconventional Types for Nonferrous Metals

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CHROMATE CONVERSION COATING PROCESSES OF THE CONVENTIONAL AND NONCONVENTIONAL TYPES FOR NONFERROUS METALS

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Because aluminum is an extremely versatile metal, its domestic and industrial use continues to grow at a steady rate. An additional reason for aluminum's expanding popularity is that aluminum can be pretreated through the same processes that steel and galvanized steel undergo. Thus, aluminum and its alloys can be pretreated for organic finishing through a multi-metal amorphous phosphate or zinc phosphate system. However, the thrust of this talk will be conventional and nonconventional chromate conversion coatings which not only serve to protect nonferrous metals, primarily aluminum and galvanized steel, abainst corrosion but also serve as an excellent bond for the adhesion of paints and adhesives.

The two most common specifications that chromate conversion coatings must meet are: ASTM-B-449 and MIL-C-5541C. The basic cycle needed to achieve standard conversion coatings that conform to these two specifications is given in Figure 1.

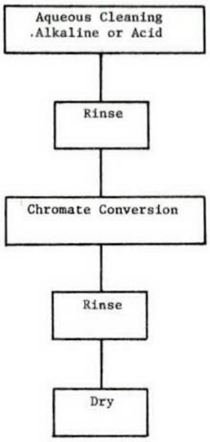

Figure 1

Although it is said that the normal soils found on fabricated aluminum are fairly easy to remove, you must always remember that aluminum and, for the most part, galvanized steel are very reactive and both metals are amphoteric. They react with many soils to form organo-metallic insolubles and their surfaces are easily etched by both soils and cleaners. The quality of an organic finish on aluminum will always be proven by the service it provides. Essentially most finishes are intended for protection, as well as beauty, and in most cases aluminum is used in exterior applications. When properly prepared, aluminum and zinc will accept almost any kind of superimposed finish.

A clean, essentially inert surface is desired or often required to provide optimum adhesion and stability. Production metals are never clean and most finishing techniques possess poor wetting out abilities. This is true of plating and also of powder coatings, high solid paints and, in many cases, waterborne systems. Thus, for proper bonding, cleaning is essential. Any interference, chemical or physical, will weaken the bond between the finish and the nonferrous substrate. Even though such a defect may be initially concealed, the soiled area will cause a deterioration of the finish and eventually attack the substrate itself.

Among the commonly employed cleaning techniques are vapor degreasing and mechanical finishing. Vapor degreasing only removes oils and other petroleum soils. But many soils found on nonferrous metals are fatty, soapy or solid. If vapor degreasing is used for parts with soils other than the petroleum type, degreasing often leaves "baked-on" residues. Abrasive blasting with glass or silica usually 40-80 mesh, can also be used to clean aluminum. Light soils can be removed and this method of surface preparation leaves an anchor profile of about 1 mil in depth.

However, here again, heavily soiled areas must be cleaned prior to blasting if the quality finish is to be expected. In addition, abrasive blasting is not only time consuming and labor intensive, but blasting is also very wasteful of sound metal.

The three parts of every cleaning puzzle are: 1. The metal surface which includes oxide formations. 2. The variety of shop soils. 3. The cleaning method along with the application procedure. A total system approach, cleaner vs. soil, application method vs. surface area to be finished, and mechanical vs. chemical must be considered in order to determine the best production procedure. The largest problem that we encounter is the unlimited combinations of soil in a production shop. Liquid and solid soils are quite different mechanisms. Because of this wide range in the type and the extent of the soils on nonferrous metals, aqueous cleaners are generally the most effective and the most economical.

Keeping in mind the sensitivity of nonferrous metals and the variety of soils encountered, non-etch cleaners are preferred. Non-etch cleaners are of the non-silicated type and possess a mild pH, usually below a pH of 10.0. They are highly buffered and are available for either spray or tank systems. These non-silicated alkaline cleaners generally possess excellent wetting out abilities and can therefore by used at fairly low temperatures. Since these alkaline cleaners are not inhibited, the common operating temperature does not normally exceed 150°F. Aluminum is never found in a nonoxidized state and an added benefit from some of these non-silicated cleaners is their ability to offer light deoxidation which helps to develope a more uniform chromate conversion coating.

Silicated alkaline cleaners are inhibited and therefore can be higher in alkalinity, up to and including a pH of 12.0, and can also be operated at higher temperatures, up to and including 200°F. For soils which require saponification, the higher degree of alkalinity and temperature often makes silicated cleaners more heavy duty. Thus, alkaline cleaners for nonferrous metals provide a wide choice in the degree of alkalinity and temperature ranges to accomodate the various soils and oxide states of metals.

Under certain conditions, such as ground-in soils which include roll formed nonferrous metals, sanded nonferrous metals and buffed nonferrous metals, cleaning can be improved by providing a controlled attack rate on the substrate. Light etching helps to dislodge ground-in particulate matter and the hydrogen gas formed during etching provides a slight degree of scrubbing action. However, in the case of a quality standard chromate conversion coating, etching of aluminum surfaces is considered poor production practice since it tends to reduce the overall protective qualities of chromate conversion coatings, e.g., salt spray resistance. Since we wish to avoid fairly heavy etching in order to obtain a high degree of corrosion resistance, acidic cleaners should be discussed. Acid cleaners are not commonly used when the primary requirement is soil removal, because they are less effective than most alkaline systems. Acidic cleaners are employed most often to level out or remove surface oxides from nonferrous metals as well as surface smut deposits. Cleaners containing phosphoric acid and fluorides are able to dissolve not only oxide films, but also oxidation products which develope in humid storage conditions or during heat treatment. Their cleaning abilities can be greatly improved through the use of synergistic blends of wetting agents and solvents. The actual etch can be very closely controlled through the use of proper concentrations, temperatures and time cycles. Acidic cleaners designed for additional etching can be based on sulfuric acid and occasionally nitric acid with or without the fluoride assist. These acid cleaners, as a group, develope a micro-etch and like alkaline etch cleaners, they are capable of producing a light satin finish with no-to-very-little alloying smut. Often, this light etch can be used from a quality control standpoint because if the surface is very uniform, all traces of organic soils must have been removed. Under precisely controlled conditions, acidic cleaners can be used with a high degree of success prior to chromate conversion coatings and also adhesive bonding.

Cleaning and surface conditioning or controlled etching develope good-to-excellent adhesion but do little for severe corrosion resistance. The selection of a final finish will depend upon the end-use requirements for the nonferrous metals. Organic finishes derive their physical and chemical properties from the nature of the polymer as well as the molecular weight of the polymer. Likewise, the total finish obtains its long term surface life from the proper conversion coating. Quality finishing demands a conversion coating which provides an inert bridge between the metal and the organic finish. A conversion coating describes the surface film formed by the reaction in which a portion of the base metal is converted to one of the components of the film. As a result, the film becomes an integral part of the metal surface, exhibiting excellent adhesion properties. The most widely employed amorphous chromate conversion coatings are generally applied from acid solutions and they are nonporous, gel-like structures containing hexavalent chrome, trivalent chrome and oxides of the base metal being coated. The fact that these coatings contain high quantities of hexavalent chrome highlights their highly corrosion resistant nature and the leachable hexavalent chrome gives them a self-healing characteristic preventing corrosion when the coating itself is damaged.

Present day conversion coatings for aluminum of the acid chromate type have three major constituents:

1. Acid chromates
2. Acidic etchant
3. Accelerator or complexing agent

The acid chromates are usually chromic acid and sodium or potassium dichromates. These provide the bulk of the coating. The etchants are acidic silicofluorides, fluorides or fluoroborates and provide the biting action into the aluminum surface without vigorous heating of the coating solution. Their extreme activity also overcomes the natural inhibition of the acid chromates on aluminum or other nonferrous surfaces. The last and the smallest constituent, but equal in importance, is the accelerator. These are proprietary and are widely varied in nature, usually metallic inorganic compounds and complexed with trivalent chromium iron. The basic reaction then is the pickling of the nonferrous metal, a resulting pH increase or reduction in acidity at the solution-metal interface with the subsequent coating being developed. Where zinc is being chromated, ferricyanide accelerators are not normally used since they form insoluble zinc salts. The other additional bath modification is the absence of the fluoride ion with other proprietary activators being used. The controls for chromate conversion coatings are listed in Figure 2.

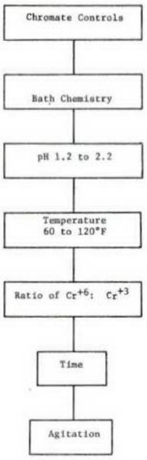

Figure 2

As stated above, the base metal, including various aluminum alloys, must be considered with respect to conditioning of the metal itself and the bath chemistry. Different chromate baths may require a specific pH range for maximum coating deposition and performance. Lighter coatings, such as colorless coatings, offer less enveloping or physical barriers and have less corrosion resistance than the gold, gold iridescent or brownish heavy coatings. For zinc plated work, galvanized steel and cadium plated parts, the pH of the chromate bath is generally low, approximately 1.2. As the pH is lowered, the bath becomes more aggressive on the base metal and the reaction products stay soluble, tending to reduce the coating weight or thickness. Excessively high pHs, beyond suggested operating parameters, reduce the rate of metal attack to a point where the reaction ceases and a powdery coating of poor quality or no coating forms. Chromating baths can be made more active to accommodate varying metal activities by increasing the temperature. The ratio of hexavalent chrome to trivalent chrome is important and is usually maintained by supplier recommendations which include specialized upkeep compounds along with a bleedoff to eliminate the trivalent chrome contamination buildup which is a natural byproduct of the solution's reaction with the base metals. Time is fairly self explanatory in that longer times generally product heavier coatings. Agitation of the solution, spray washer applications in general, result in fresh solution contacting the work surface.

This speeds up the reaction and provides heavier coatings in a shorter time and perhaps a somewhat more uniform film formation.

Standard conversion coatings can be used with and without paints for a high degree of corrosion protection. Where aluminum always receives a paint film, amorphous chrome phosphate coatings can be substituted. Amorphous chrome phosphate coatings are also produced in acid solutions but these solutions contain phosphoric acid, hexavalent and trivalent chrome, and fluorides. They are the most widely used conversion coatings for aluminum extrusions and are used almost exclusively for architectural exterior products. The resulting film is primarily chrome phosphate and aluminum phosphate and the color is a characteristic green from its reduced chrome content. The conditioning cycle for the aluminum is slightly different and set forth in Figure 3.

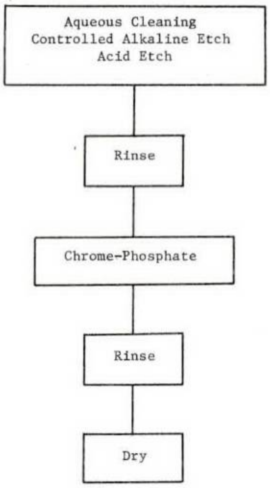

Figure 3

Since aluminum extrusions generally contain a heavy non-uniform oxide skin, some metal removal by controlled alkaline etch cleaning or acid cleaning is necessary, if not highly desirable. The chrome phosphate controls are also slightly different and they are listed in Figure 4.

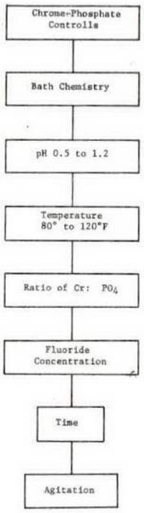

Figure 4

The bath composition may change slightly from one supplier to another. As you can see, the pH of a chrome phosphate solution is generally lower than standard chromates and this allows additional attack or oxide removal in the conversion coating solution itself. Temperature is not critical and the average is 100°F. The ratio of chrome to phosphate is fairly wide providing the pH is correct for the coating weight desired. The fluoride concentration is replenished along with the chrome and phosphate levels. For short treatment times, several seconds, fluoride concentration is increased. If exposure times can be lengthened, the fluoride level can be less. Supplier recommendations should again be closely followed. The fluoride level in the operating solution enables the user to effectively dissolve surface oxides from difficult to coat aluminum extrusions and castings due to the bath's considerable activity which makes initial conditioning treatments somewhat less critical.

Pretreatments, such as the two just discussed, are essentially five sided:

1. They remove soils and surface imperfections
2. They create bonding sites
3. They establish a corrosion barrier
4. They neutralize surface pH changes
5. They do all four functions economically

To help industry combat pollution and keep the high performance benefits of chromates, no-rinse reactive chromates are being used in production. These new active prepaint treatments do not form the troublesome soluble solution byproducts. Therefore, rinsing is not required--no rinsing, no pollution. Exposure time of nonferrous metals to these solutions is not a factor. The solutions are used at ambient temperatures, although they can be heated to facilitate the reaction which takes place during curing. The treatment requires no on-the-job chemical balancing such as adjustment of hexavalent to trivalent chrome and fluoride levels. These reactive no-rinse pretreatments must be applied to clean, waterbreak-free surfaces and again aqueous cleaning is required. Cleaners must be tailored to the soils and also offer compatability with the particular no-rinse treatment being applied. Similar to chromates and chrome phosphate, the application is generally by spray or flow on, but immersion is also possible. These no-rinse prepaint treatments have multimetal capabilities and when combined with the proper organic finish, they can meet very stringent corrosion requirements such as the AEMA Specifications.

The quality of aluminum finished with an organic coating is a direct reflection of the prepaint system, the paint's characteristics, the operator's experience, and his conscientious observance of the proper processing procedures. In the next several years, industrial finishers will be faced with the need to improve quality, reduce pollution and conserve materials. Chromates are still required in many application because of their high performance properties.


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