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# Natural Green Corrosion Inhibitors for Metal Surfaces

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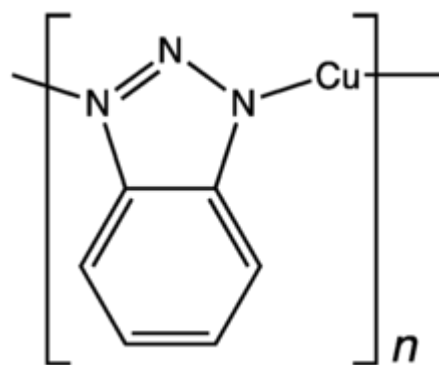
**ABSTRACT:** In chemistry, a corrosion inhibitor or anti-corrosive is a chemical compound that, when added to a liquid or gas, decreases the corrosion rate of a material, typically a metal or an alloy, that comes into contact with the fluid.<sup>[1]</sup> The effectiveness of a corrosion inhibitor depends on fluid composition, quantity of water, and flow regime. Corrosion inhibitors are common in industry, and also found in over-the-counter products, typically in spray form in combination with a lubricant and sometimes a penetrating oil. They may be added to water to prevent leaching of lead or copper from pipes.<sup>[2]</sup>

A common mechanism for inhibiting corrosion involves formation of a coating, often a passivation layer, which prevents access of the corrosive substance to the metal. Permanent treatments such as chrome plating are not generally considered inhibitors, however: corrosion inhibitors are additives to the fluids that surround the metal or related object.

**KEYWORDS:** natural, inhibitors, metal surfaces, corrosion, green, chemical, chrome, oil, coating

## I. INTRODUCTION

The nature of the corrosive inhibitor depends on (i) the material being protected, which are most commonly metal objects, and (ii) on the corrosive agent(s) to be neutralized. The corrosive agents are generally oxygen, hydrogen sulfide, and carbon dioxide. Oxygen is generally removed by reductive inhibitors such as amines and hydrazines:



Benzotriazole inhibits corrosion of copper by forming an inert layer of this polymer on the metal's surface

In this example, hydrazine converts oxygen, a common corrosive agent, to water, which is generally benign. Related inhibitors of oxygen corrosion are hexamine, phenylenediamine, and dimethylethanolamine, and their derivatives. Antioxidants such as sulfite and ascorbic acid are sometimes used. Some corrosion inhibitors form a passivating coating on the surface by chemisorption. Benzotriazole is one such species used to protect copper. For lubrication, zinc dithiophosphates are common - they deposit sulfide on surfaces.

The suitability of any given chemical for a task in hand depends on many factors, including their operating temperature.<sup>[3]</sup>

### Illustrative applications

- Volatile amines are used in boilers to minimize the effects of acid. In some cases, the amines form a protective film on the steel surface and, at the same time, act as an anodic inhibitor. An inhibitor that acts both in a cathodic and anodic manner is termed a mixed inhibitor.

- Benzotriazole inhibits the corrosion and staining of copper surfaces.<sup>[4]</sup>
- Corrosion inhibitors are often added to paints. A pigment with anticorrosive properties is zinc phosphate. Compounds derived from tannic acid or zinc salts of organonitrogens (e.g. Alcophor 827) can be used together with anticorrosive pigments. Other corrosion inhibitors are Anticor 70, Albaex, Ferrophos, and Molywhite MZAP.
- Antiseptics are used to counter microbial corrosion. Benzalkonium chloride is commonly used in oil field industry.
- In oil refineries, hydrogen sulfide can corrode steels so it is removed often using air and amines by conversion to polysulfides.
- Orthophosphates may be added in water treatment systems to prevent leaching of lead and copper from pipes.<sup>[2]</sup>

#### Fuels industry

Corrosion inhibitors are commonly added to coolants, fuels, hydraulic fluids, boiler water, engine oil, and many other fluids used in industry. For fuels, various corrosion inhibitors can be used. Some components include zinc dithiophosphates.<sup>[5]</sup>

- DCI-4A, widely used in commercial and military jet fuels, acts also as a lubricity additive. Can be also used for gasolines and other distillate fuels.
- DCI-6A, for motor gasoline and distillate fuels, and for U.S. military fuels (JP-4, JP-5, JP-8)
- DCI-11, for alcohols and gasolines containing oxygenates
- DCI-28, for very low-pH alcohols and gasolines containing oxygenates
- DCI-30, for gasoline and distillate fuels, excellent for pipeline transfers and storage, caustic-resistant
- DMA-4 (solution of alkylaminophosphate in kerosene), for petroleum distillates

Corrosion is a natural process that converts a refined metal into a more chemically stable oxide. It is the gradual deterioration of materials (usually a metal) by chemical or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen, hydrogen or hydroxide. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal and results in a distinctive orange coloration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term "degradation" is more common. Corrosion degrades the useful properties of materials and structures including mechanical strength, appearance, and permeability to liquids and gases.

Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area, more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

The chemistry of corrosion is complex; it can be considered an electrochemical phenomenon. During corrosion at a particular spot on the surface of an object made of iron, oxidation takes place and that spot behaves as an anode. The electrons released at this anodic spot move through the metal to another spot on the object, and reduce oxygen at that spot in presence of H<sup>+</sup> (which is believed to be available from carbonic acid (H<sub>2</sub>CO<sub>3</sub>) formed due to dissolution of carbon dioxide from air into water in moist air condition of atmosphere. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as a cathode.

High-temperature corrosion is chemical deterioration of a material (typically a metal) as a result of heating. This non-galvanic form of corrosion can occur when a metal is subjected to a hot atmosphere containing oxygen, sulfur ("sulfidation"), or other compounds capable of oxidizing (or assisting the oxidation of) the material concerned. For example, materials used in aerospace, power generation, and even in car engines must resist sustained periods at high temperature, during which they may be exposed to an atmosphere containing the potentially highly-corrosive products of combustion.



Some products of high-temperature corrosion can potentially be turned to the advantage of the engineer. The formation of oxides on stainless steels, for example, can provide a protective layer preventing further atmospheric attack, allowing for a material to be used for sustained periods at both room and high temperatures in hostile conditions. Such high-temperature corrosion products, in the form of compacted oxide layer glazes, prevent or reduce wear during high-temperature sliding contact of metallic (or metallic and ceramic) surfaces. Thermal oxidation is also commonly used to produce controlled oxide nanostructures, including nanowires and thin films.

Microbial corrosion, or commonly known as microbiologically influenced corrosion (MIC), is a corrosion caused or promoted by microorganisms, usually chemoautotrophs. It can apply to both metallic and non-metallic materials, in the presence or absence of oxygen. Sulfate-reducing bacteria are active in the absence of oxygen (anaerobic); they produce hydrogen sulfide, causing sulfide stress cracking. In the presence of oxygen (aerobic), some bacteria may directly oxidize iron to iron oxides and hydroxides, other bacteria oxidize sulfur and produce sulfuric acid causing biogenic sulfide corrosion. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

Accelerated low-water corrosion (ALWC) is a particularly aggressive form of MIC that affects steel piles in seawater near the low water tide mark. It is characterized by an orange sludge, which smells of hydrogen sulfide when treated with acid. Corrosion rates can be very high and design corrosion allowances can soon be exceeded leading to premature failure of the steel pile.<sup>[5]</sup> Piles that have been coated and have cathodic protection installed at the time of construction are not susceptible to ALWC. For unprotected piles, sacrificial anodes can be installed locally to the affected areas to inhibit the corrosion or a complete retrofitted sacrificial anode system can be installed. Affected areas can also be treated using cathodic protection, using either sacrificial anodes or applying current to an inert anode to produce a calcareous deposit, which will help shield the metal from further attack.

## II. DISCUSSION

When surface treatments are used to deter corrosion, great care must be taken to ensure complete coverage, without gaps, cracks, or pinhole defects. Small defects can act as an "Achilles' heel", allowing corrosion to penetrate the interior and causing extensive damage even while the outer protective layer remains apparently intact for a period of time.

Applied coatings



Galvanized surface



### Corroding steel gantry on an electrified railway line

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the structural material. Aside from cosmetic and manufacturing issues, there may be tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, but if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with active metal such as zinc or cadmium. If the zinc coating is not thick enough the surface soon becomes unsightly with rusting obvious. The design life is directly related to the metal coating thickness.

Painting either by roller or brush is more desirable for tight spaces; spray would be better for larger coating areas such as steel decks and waterfront applications. Flexible polyurethane coatings, like Durabak-M26 for example, can provide an anti-corrosive seal with a highly durable slip resistant membrane. Painted coatings are relatively easy to apply and have fast drying times although temperature and humidity may cause dry times to vary. Nowadays, organic coatings made using petroleum based polymer are being replaced with many renewable source based organic coatings. Among various vehicles or binders, polyurethanes are the most explored polymer in such a attempts.<sup>[6]</sup>

### Reactive coatings

If the environment is controlled (especially in recirculating systems), corrosion inhibitors can often be added to it. These chemicals form an electrically insulating or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts in hard water (Roman water systems are known for their mineral deposits), chromates, phosphates, polyaniline, other conducting polymers and a wide range of specially designed chemicals that resemble surfactants (i.e. long-chain organic molecules with ionic end groups).

### Anodization



This climbing descender is anodized with a yellow finish.

Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores, several nanometers wide, appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow. At the end of the treatment, the pores are allowed to seal, forming a harder-than-usual surface layer. If this coating is scratched, normal passivation processes take over to protect the damaged area.

Anodizing is very resilient to weathering and corrosion, so it is commonly used for building facades and other areas where the surface will come into regular contact with the elements. While being resilient, it must be cleaned frequently. If left without cleaning, panel edge staining will naturally occur. Anodization is the process of converting an anode into cathode by bringing a more active anode in contact with it.

### Biofilm coatings

A new form of protection has been developed by applying certain species of bacterial films to the surface of metals in highly corrosive environments. This process increases the corrosion resistance substantially. Alternatively, antimicrobial-producing biofilms can be used to inhibit mild steel corrosion from sulfate-reducing bacteria.<sup>[7]</sup>

### III. RESULTS

CRC Industries is a manufacturer and distributor of industrial chemicals for maintenance and repair of marine, electrical, industrial, automotive and aviation equipment.<sup>[1][2]</sup>

It was founded in 1958 after a verbal agreement between Rocket Chemical, the predecessor of the WD-40 Company, and Charles J. Webb II to distribute WD-40 fell apart. Webb then set up a competitor company in Philadelphia, Corrosion Reaction Consultants, Inc., and hired away Rocket president Norman Larsen to lead it.<sup>[3]</sup> In 1960 it consisted of Larsen, two chemists and five staff.<sup>[4]</sup> Its first product was CRC Corrosion Inhibitor, also called 5-56, a product comparable to WD-40. The product was reformulated in 1963 as the company diversified to make more specialized products.<sup>[3]</sup>

The company has been owned by Berwind Corporation since 1981.<sup>[3]</sup> CRC's first product, 5-56, is still sold. However, 6-56, a silicone-based replacement, is CRC's current competing product for WD-40.<sup>[5]</sup>

Brakleen, a tetrachloroethylene (PERC)-based brake cleaner, is one of CRC's signature products. It has gained a cult following due to its dissolving power and has been used off-label for many other purposes, a practice strongly discouraged by health experts and the product's own warning labels. As PERC is illegal in New Jersey and California, a safer but weaker substitute chlorine-free formula mostly made of acetone and heptane is also offered.<sup>[6]</sup>

CRC's manufacturing is headquartered in Warminster, Pennsylvania with the corporate office in Horsham, Pennsylvania. It markets products through subsidiaries in the United States, Australia, Germany,<sup>[7]</sup> Belgium, United Kingdom, China and New Zealand.<sup>[1][2]</sup>

Their facilities in Warminster include a private railroad spur, served by the New Hope Railroad. Traffic on the spur constitutes a sizable portion of the railroad's freight traffic; CRC Industries is their largest freight customer.

Hot-dip galvanization is a form of galvanization. It is the process of coating iron and steel with zinc, which alloys with the surface of the base metal when immersing the metal in a bath of molten zinc at a temperature of around 450 °C (842 °F). When exposed to the atmosphere, the pure zinc (Zn) reacts with oxygen (O<sub>2</sub>) to form zinc oxide (ZnO), which further reacts with carbon dioxide (CO<sub>2</sub>) to form zinc carbonate (ZnCO<sub>3</sub>), a usually dull grey, fairly strong material that protects the steel underneath from further corrosion in many circumstances. Galvanized steel is widely used in applications where corrosion resistance is needed without the cost of stainless steel, and is considered superior in terms of cost and life-cycle. It can be identified by the crystallization patterning on the surface (often called a "spangle").<sup>[1]</sup>

Galvanized steel can be welded; however, one must exercise caution around the resulting toxic zinc fumes. Galvanized fumes are released when the galvanized metal reaches a certain temperature. This temperature varies by the galvanization process used. In long-term, continuous exposure, the recommended maximum temperature for hot-dip galvanized steel is 200 °C (392 °F), according to the American Galvanizers Association. The use of galvanized steel at temperatures above this will result in peeling of the zinc at the inter-metallic layer. Electro-galvanized sheet steel is often used in automotive manufacturing to enhance the corrosion performance of exterior body panels; this is, however, a completely different process which tends to achieve lower coating thicknesses of zinc.

Like other corrosion protection systems, galvanizing protects steel by acting as a barrier between steel and the atmosphere. However, zinc is a more electropositive (active) metal in comparison to steel. This is a unique characteristic for galvanizing, which means that when a galvanized coating is damaged and steel is exposed to the atmosphere, zinc can continue to protect steel through galvanic corrosion (often within an annulus of 5 mm, above which electron transfer rate decreases).

#### Process

The process of hot-dip galvanizing results in a metallurgical bond between zinc and steel, with a series of distinct iron-zinc alloys. The resulting coated steel can be used in much the same way as uncoated.

A typical hot-dip galvanizing line operates as follows:<sup>[2]</sup>

- Steel is cleaned using a caustic solution. This removes oil/grease, dirt, and paint.
- The caustic cleaning solution is rinsed off.
- The steel is pickled in an acidic solution to remove mill scale.
- The pickling solution is rinsed off.

- A flux, often zinc ammonium chloride is applied to the steel to inhibit oxidation of the cleaned surface upon exposure to air. The flux is allowed to dry on the steel and aids in the process of the liquid zinc wetting and adhering to the steel.
- The steel is dipped into the molten zinc bath and held there until the temperature of the steel equilibrates with that of the bath.
- The steel is cooled in a quench tank to reduce its temperature and inhibit undesirable reactions of the newly formed coating with the atmosphere.

Lead is often added to the molten zinc bath to improve the fluidity of the bath (thus limiting excess zinc on the dipped product by improved drainage properties), help prevent floating dross, make dross recycling easier and protect the kettle from uneven heat distribution from the burners. Environmental regulations in the United States disapprove of lead in the kettle bath. Lead is either added to primary Z1 grade zinc or already contained in used secondary zinc. A third, declining method is to use low Z5 grade zinc.<sup>[3]</sup>

Steel strip can be hot-dip galvanized in a continuous line. Hot-dip galvanized steel strip (also sometimes loosely referred to as galvanized iron) is extensively used for applications requiring the strength of steel combined with the resistance to corrosion of zinc, such as roofing and walling, safety barriers, handrails, consumer appliances and automotive body parts. One common use is in metal pails. Galvanized steel is also used in most heating and cooling duct systems in buildings

Individual metal articles, such as steel girders or wrought iron gates, can be hot-dip galvanized by a process called batch galvanizing. Other modern techniques have largely replaced hot-dip for these sorts of roles. This includes electrogalvanizing, which deposits the layer of zinc from an aqueous electrolyte by electroplating, forming a thinner and much stronger bond.

A hot-dip galvanized coating is relatively easier and cheaper to specify than an organic paint coating of equivalent corrosion protection performance. The British, European and International standard for hot-dip galvanizing is BS EN ISO 1461, which specifies a minimum coating thickness to be applied to steel in relation to the steel's section thickness e.g. a steel fabrication with a section size thicker than 6 mm shall have a minimum galvanized coating thickness of 85  $\mu\text{m}$ .

Further performance and design information for galvanizing can be found in BS EN ISO 14713-1 and BS EN ISO 14713-2. The durability performance of a galvanized coating depends solely on the corrosion rate of the environment in which it is placed. Corrosion rates for different environments can be found in BS EN ISO 14713-1, where typical corrosion rates are given, along with a description of the environment in which the steel would be used.

Plating is a surface covering in which a metal is deposited on a conductive surface. Plating has been done for hundreds of years; it is also critical for modern technology. Plating is used to decorate objects, for corrosion inhibition, to improve solderability, to harden, to improve wearability, to reduce friction, to improve paint adhesion, to alter conductivity, to improve IR reflectivity, for radiation shielding, and for other purposes. Jewelry typically uses plating to give a silver or gold finish.

Thin-film deposition has plated objects as small as an atom,<sup>[1]</sup> therefore plating finds uses in nanotechnology.

There are several plating methods, and many variations. In one method, a solid surface is covered with a metal sheet, and then heat and pressure are applied to fuse them (a version of this is Sheffield plate). Other plating techniques include electroplating, vapor deposition under vacuum and sputter deposition. Recently, plating often refers to using liquids. Metallizing refers to coating metal on non-metallic objects.

### Electroplating

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In electroplating, an ionic metal is supplied with electrons to form a non-ionic coating on a substrate. A common system involves a chemical solution with the ionic form of the metal, an anode (positively charged) which may consist of the metal being plated (a soluble anode) or an insoluble anode (usually carbon, platinum, titanium, lead, or steel), and finally, a cathode (negatively charged) where electrons are supplied to produce a film of non-ionic metal.

### Electroless Deposition

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Electroless deposition, also known as chemical or auto-catalytic plating, is a non-galvanic plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by a reducing agent, normally sodium hypophosphite (Note: the

hydrogen leaves as a hydride ion) or thiourea, and oxidized, thus producing a negative charge on the surface of the part. The most common electroless deposition method is electroless nickel plating, although silver, gold and copper layers can also be applied in this manner, as in the technique of angel gilding.

#### Gold plating

Gold plating is a method of depositing a thin layer of gold on the surface of glass or metal, most often copper or silver.

Gold plating is often used in electronics, to provide a corrosion-resistant electrically conductive layer on copper, typically in electrical connectors and printed circuit boards. With direct gold-on-copper plating, the copper atoms have the tendency to diffuse through the gold layer, causing tarnishing of its surface and formation of an oxide/sulfide layer. Therefore, a layer of a suitable barrier metal, usually nickel, has to be deposited on the copper substrate, forming a copper-nickel-gold sandwich.

Metals and glass may also be coated with gold for ornamental purposes, using a number of different processes usually referred to as gilding.

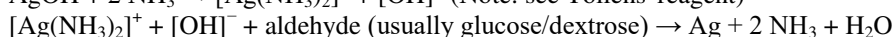
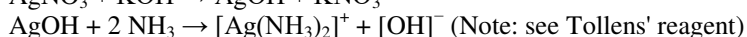
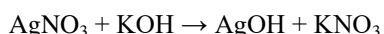
Sapphires, plastics, and carbon fiber are some other materials that are able to be plated using advance plating techniques. The substrates that can be used are almost limitless.<sup>[2]</sup>

#### Silver plating

Silver plating has been used since the 18th century to provide cheaper versions of household items that would otherwise be made of solid silver, including cutlery, vessels of various kinds, and candlesticks. In the UK the assay offices, and silver dealers and collectors, use the term "silver plate" for items made from solid silver, derived long before silver plating was invented from the Spanish word for silver "plata", seizures of silver from Spanish ships carrying silver from America being a large source of silver at the time. This can cause confusion when talking about silver items; plate or plated. In the UK it is illegal to describe silver-plated items as "silver". It is not illegal to describe silver-plated items as "silver plate", although this is ungrammatical.

The earliest form of silver plating was Sheffield Plate, where thin sheets of silver are fused to a layer or core of base metal, but in the 19th century new methods of production (including electroplating) were introduced. Britannia metal is an alloy of tin, antimony and copper developed as a base metal for plating with silver.

Another method that can be used to apply a thin layer of silver to objects such as glass, is to place Tollens' reagent in a glass, add glucose/dextrose, and shake the bottle to promote the reaction.



For applications in electronics, silver is sometimes used for plating copper, as its electrical resistance is lower (see Resistivity of various materials); more so at higher frequencies due to the skin effect. Variable capacitors are considered of the highest quality when they have silver-plated plates. Similarly, silver-plated, or even solid silver cables, are prized in audiophile applications; however some experts consider that in practice the plating is often poorly implemented, making the result inferior to similarly priced copper cables.<sup>[3]</sup>

Care should be used for parts exposed to high humidity environments because in such environments, when the silver layer is porous or contains cracks, the underlying copper undergoes rapid galvanic corrosion, flaking off the plating and exposing the copper itself; a process known as red plague. Silver plated copper maintained in a moisture-free environment will not undergo this type of corrosion.

#### Copper plating

Copper plating is the process of electrolytically forming a layer of copper on the surface of an item. It is commonly used as an even cheaper alternative to silver plating as it is much cheaper than silver.

#### Rhodium plating

Rhodium plating is occasionally used on white gold, silver or copper and its alloys. A barrier layer of nickel is usually deposited on silver first, though in this case it is not to prevent migration of silver through rhodium, but to prevent contamination of the rhodium bath with silver and copper, which slightly dissolve in the sulfuric acid usually present in the bath composition.<sup>[4]</sup>



### Chrome plating

Chrome plating is a finishing treatment using the electrolytic deposition of chromium. The most common form of chrome plating is the thin, decorative bright chrome, which is typically a 10- $\mu\text{m}$  layer over an underlying nickel plate. When plating on iron or steel, an underlying plating of copper allows the nickel to adhere. The pores (tiny holes) in the nickel and chromium layers work to alleviate stress caused by thermal expansion mismatch but also hurt the corrosion resistance of the coating. Corrosion resistance relies on what is called the passivation layer, which is determined by the chemical composition and processing, and is damaged by cracks and pores. In a special case, micropores can help distribute the electrochemical potential that accelerates galvanic corrosion between the layers of nickel and chromium. Depending on the application, coatings of different thicknesses will require different balances of the aforementioned properties. Thin, bright chrome imparts a mirror-like finish to items such as metal furniture frames and automotive trim. Thicker deposits, up to 1000  $\mu\text{m}$ , are called hard chrome and are used in industrial equipment to reduce friction and wear.

The traditional solution used for industrial hard chrome plating is made up of about 250 g/L of  $\text{CrO}_3$  and about 2.5 g/L of  $\text{SO}_4^-$ . In solution, the chrome exists as chromic acid, known as hexavalent chromium. A high current is used, in part to stabilize a thin layer of chromium(+2) at the surface of the plated work. Acid chrome has poor throwing power, fine details or holes are further away and receive less current resulting in poor plating.

### Zinc plating

Zinc coatings prevent oxidation of the protected metal by forming a barrier and by acting as a sacrificial anode if this barrier is damaged. Zinc oxide is a fine white dust that (in contrast to iron oxide) does not cause a breakdown of the substrate's surface integrity as it is formed. Indeed, the zinc oxide, if undisturbed, can act as a barrier to further oxidation, in a way similar to the protection afforded to aluminum and stainless steels by their oxide layers. The majority of hardware parts are zinc-plated, rather than cadmium-plated.<sup>[5]</sup>

### Zinc-nickel plating

Zinc-nickel plating is one of the best corrosion resistant finishes available offering over 5 times the protection of conventional zinc plating and up to 1,500 hours of neutral salt spray test performance. This plating is a combination of a high-nickel zinc-nickel alloy (10–15% nickel) and some variation of chromate. The most common mixed chromates include hexavalent iridescent, trivalent or black trivalent chromate. Used to protect steel, cast iron, brass, copper, and other materials, this acidic plating is an environmentally safe option.<sup>[6]</sup> Hexavalent chromate has been classified as a human carcinogen by the EPA and OSHA.<sup>[7][8]</sup>

### Tin plating

The tin-plating process is used extensively to protect both ferrous and nonferrous surfaces. Tin is a useful metal for the food processing industry since it is non-toxic, ductile and corrosion resistant. The excellent ductility of tin allows a tin coated base metal sheet to be formed into a variety of shapes without damage to the surface tin layer. It provides sacrificial protection for copper, nickel and other non-ferrous metals, but not for steel.

Tin is also widely used in the electronics industry because of its ability to protect the base metal from oxidation thus preserving its solderability. In electronic applications, 3% to 7% lead may be added to improve solderability and to prevent the growth of metallic "whiskers" in compression stressed deposits, which would otherwise cause electrical shorting. However, RoHS (Restriction of Hazardous Substances) regulations enacted beginning in 2006 require that no lead be added intentionally and that the maximum percentage not exceed 1%. Some exemptions have been issued to RoHS requirements in critical electronics applications due to failures which are known to have occurred as a result of tin whisker formation.

### Alloy plating

In some cases, it is desirable to co-deposit two or more metals resulting in an electroplated alloy deposit. Depending on the alloy system, an electroplated alloy may be solid solution strengthened or precipitation hardened by heat treatment to improve the plating's physical and chemical properties. Nickel-Cobalt is a common electroplated alloy.

### Composite plating

Metal matrix composite plating can be manufactured when a substrate is plated in a bath containing a suspension of ceramic particles. Careful selection of the size and composition of the particles can fine-tune the deposit for wear resistance, high temperature performance, or mechanical strength. Tungsten carbide, silicon carbide, chromium carbide, and aluminum oxide (alumina) are commonly used in composite electroplating.

### Cadmium plating

Cadmium plating is under scrutiny because of the environmental toxicity of the cadmium metal. Cadmium plating is widely used in some applications in the aerospace, military, and aviation fields. However, it is being phased out due to its toxicity.<sup>[9]</sup> Military and Aerospace components manufacturers, such as Amphenol Aerospace, have recently been exploring drop-in electroplating replacements for use with currently fielded equipment in order to support the phaseout of the dangerous finish.<sup>[10]</sup>

Cadmium plating (or cad. plating) offers a long list of technical advantages such as excellent corrosion resistance even at relatively low thickness and in salt atmospheres, softness and malleability, freedom from sticky and/or bulky corrosion products, galvanic compatibility with aluminum, freedom from stick-slip thus allowing reliable torquing of plated threads, can be dyed to many colors and clear, has good lubricity and solderability, and works well either as a final finish or as a paint base.<sup>[5][11]</sup>

If environmental concerns matter, in most aspects cadmium plating can be directly replaced with gold plating as it shares most of the material properties, but gold is more expensive and cannot serve as a paint base.

### Nickel plating

Nickel is electroplated by using a Watts bath, an electrolytic cell having a nickel anode and electrolyte containing nickel sulfate, nickel chloride, and boric acid.<sup>[12]</sup> Other nickel salts such as nickel ammonium sulfate are sometimes used instead of nickel sulfate.

### Electroless nickel plating

Electroless nickel plating, also known as enickel and NiP, offers many advantages: uniform layer thickness over most complicated surfaces, direct plating of ferrous metals (steel), superior wear and corrosion resistance compared to electroplated nickel or chrome. Much of the chrome plating done in aerospace industry can be replaced with electroless nickel plating, again environmental costs, costs of hexavalent chromium waste disposal and notorious tendency of uneven current distribution favor electroless nickel plating.<sup>[13]</sup>

Electroless nickel plating is self-catalyzing process, the resultant nickel layer is NiP compound, with 7–11% phosphorus content. Properties of the resultant layer hardness and wear resistance are greatly altered with bath composition and deposition temperature, which should be regulated with 1 °C precision, typically at 91 °C.

During bath circulation, any particles in it will become also nickel-plated; this effect is used to advantage in processes which deposit plating with particles like silicon carbide (SiC) or polytetrafluoroethylene (PTFE). While superior compared to many other plating processes, it is expensive because the process is complex. Moreover, the process is lengthy even for thin layers. When only corrosion resistance or surface treatment is of concern, very strict bath composition and temperature control is not required and the process is used for plating many tons in one bath at once.

Electroless nickel plating layers are known to provide extreme surface adhesion when plated properly. Electroless nickel plating is non-magnetic and amorphous. Electroless nickel plating layers are not easily solderable, nor do they seize with other metals or another electroless nickel-plated workpiece under pressure. This effect benefits electroless nickel-plated screws made out of malleable materials like titanium. Electrical resistance is higher compared to pure metal plating.

## IV. CONCLUSIONS

Mechanical plating, also known as peen plating, mechanical deposition, or impact plating, is a plating process that imparts the coating by cold welding fine metal particles to a workpiece. Mechanical galvanization is the same process, but applies to coatings that are thicker than 0.001 in (0.025 mm).<sup>[1]</sup> It is commonly used to overcome hydrogen embrittlement problems. Commonly plated workpieces include nails, screws, nuts, washers, stampings, springs, clips, and sintered iron components.<sup>[2][3]</sup>

The process involves tumbling the workpieces with a mixture of water, metal powder, media, and additives. Common coating materials are zinc, cadmium, tin, copper, and aluminium.<sup>[4]</sup>

Invented by the Tainton Company in the 1950s, it was further developed by the 3M company.<sup>[5]</sup>

The process begins with a descaling and removing soil from the workpiece. This can be done in the tumbler or in a separate cleaning system. After cleaning, the parts are prepared by combining them with water, medium, and a surface conditioner. The surface conditioner lightly coats the workpiece in copper, while the medium removes any residual mill scale or oxides. Finally, accelerators, promoters and metal powder are added to the mix. The accelerators and promoters

provide the proper chemical environment for the plating to occur, such as the maintenance of a pH level of 1 to 2 to prevent oxidation and promote adhesion. The medium that is already in the mixture cold welds the metal powder to the workpiece through impacts that are induced by the tumbling action of the tumbler. At this point the surface finish is typically matte to a semi-bright finish, however the finish can be improved with a water polish. The time required for the above process is approximately 50 minutes.<sup>[1][4]</sup>

For some thinly coated workpieces a chromate passivation is necessary. Finally, the workpiece, whether passivated or not, is dried.<sup>[4]</sup>

The medium material is usually soda lime glass or a ceramic. It is usually spherical in form, but angular shapes are also used. For plating, medium usage is usually 1 part medium for every workpiece, but for galvanization the ratio is 2:1. However, various sized media are used in each batch with a typical batch consisting of 50% 4–5 in (100–130 mm) sized beads, 25% 2–2.5 in (51–64 mm) sized beads, and 25% 1–1.25 in (25–32 mm) sized beads. The smaller media are omitted when the workpiece has a cavity that the medium can get caught in, such as a fastener's recessed head. Note that the medium is reused many times.<sup>[1][4]</sup>

This process works better if the workpieces' surface finish is slightly rough.<sup>[1]</sup>

The most important piece of equipment in the process is the tumbler. It is constructed of steel or stainless steel and lined with an acid and abrasion resistant material, such as neoprene, polypropylene, and polybutylene. The barrel sizes range from 0.04–1.13 m<sup>3</sup> (1.4–39.9 cu ft), however the working volume is only 25 to 35% of the total volume. For most plating applications the tumbler is rotated at 60 RPM, however it can vary. If the speed is too fast then lumpy deposits will form on the workpieces, but if the speed is too slow then the metal powder will not deposit onto the workpiece.

The separator separates the coated workpieces from the medium after coating. It can be as simple as a screen with water nozzles or as complicated as a vibratory system with magnetic separators. A medium handling machine then takes the separated medium and transports it to a storage tank for reuse.<sup>[4]</sup>

The separated workpieces are then taken to a dryer to remove any moisture. Usually centrifugal dryers are used, however oven are used for larger parts or loads.<sup>[4]</sup>

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