Chromium

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Chromium has recently become a hot topic. This note will cover governmental regulations, forms, uses, hazards, and other issues galvanizers may have with chromium. These include the possibility of a new OSHA regulation, the industry’s current position, and possible alternatives to chromium. In addition, this note discusses the possible exposure routes and testing methods that a galvanizing plant can use.
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Governmental Regulations

The Occupational Safety and Health Association (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) respectively specify the permissible exposure limits (PELs) and the recommended exposure limits (RELs) for hazardous substances in the workplace. The PELs are based on the feasibility of controlling the exposure to the substance in question within the workplace environment, while the RELs are based on requirements for preventing an occupational disease from occurring. Although employers are legally bound only by the PELs, they are encouraged by NIOSH to follow whichever limit is more protective. The current PEL for total chromium, in the general industry, as stated in 29 CFR 1910.1000, is 100 micrograms per cubic meter (µg/m³), as a time-weighted average (TWA), and 52 µg/m³ TWA for hexavalent chromium. The REL for hexavalent chromium compounds in the workplace air is much lower, only 1 µg/m³. This REL limit applies to all forms of hexavalent chromium, including chromic acid, chromates, lead chromate, and zinc chromate.

OSHA, the governing body that sets PEL limits, has been hesitant to lower the current standard for hexavalent chromium. In 1993 OSHA proposed to lower the PEL for hexavalent chromium after Public Citizen, a consumer group, and Paper, Allied-Industrial, Chemical and Energy Workers International Union (PACE) petitioned the agency to issue an emergency standard. In the spring of 2002, the two groups filed suit in the U.S. Court of Appeals for the Third Circuit asking the court to order OSHA to issue a proposed PEL for hexavalent chromium within 90 days, and issue a final standard within one year. The groups stated that court action was necessary because the agency had unreasonably delayed responding to the 1993 request for the PEL to be lowered to 0.5 µg/m³, which is 200 times lower than the current standard. In early 2004, the court ordered a proposed rule on workplace exposure to hexavalent chromium be issued no later than October 4, 2004, and a final ruling no later than January 18, 2006.

The EPA and the World Health Organization (WHO) have determined that hexavalent chromium in the air is a human carcinogen, and the Department of Health and
Human Services (DHHS) has determined that certain hexavalent chromium compounds are known to cause cancer in humans. Certain hexavalent chromium compounds may be harmful, but all current evidence indicates that the carcinogenicity is site-specific, limited to the lung and nasal cavity, and dependent on high exposure to hexavalent chromium, similar to what might be encountered in an industrial setting. Several studies have shown that hexavalent chromium compounds can increase the risk of lung cancer. Studies done on animals have also shown an increased risk of cancer.

This paper will define chromium, its uses, the possible dangers of over exposure to hexavalent chromium, how to minimize these dangers, and how the galvanizing industry could be affected.

**Background**

Chromium has many uses in the industrial world. It has been estimated that workers in approximately 80 different professional categories may be exposed to hexavalent chromium. Chromium is an additive that provides alloys or metals with improved properties. These properties include resistance to corrosion, wear, temperature, and/or decay. In addition, it can increase the strength, hardness, permanence, hygiene, and color of the product. Some sources of chromium emissions include oil and coal combustion, stainless steel welding, steel production, cement plants, industrial paint and coating manufacturing, and cooling towers that use hexavalent chromium as a rust inhibitor for their submerged moving parts. Occupational sources of chromium exposure may occur in the industries listed in
Table 1.
Table 1: Examples of occupations that may involve chromium exposure

<table>
<thead>
<tr>
<th>Industry</th>
<th>Chromium Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel welding</td>
<td>Hexavalent Chromium</td>
</tr>
<tr>
<td>Chromate production</td>
<td>Hexavalent Chromium</td>
</tr>
<tr>
<td>Chrome plating</td>
<td>Hexavalent Chromium</td>
</tr>
<tr>
<td>Ferrochrome industry</td>
<td>Trivalent Chromium and Hexavalent Chromium</td>
</tr>
<tr>
<td>Chrome pigments</td>
<td>Trivalent Chromium and Hexavalent Chromium</td>
</tr>
<tr>
<td>Leather tanning</td>
<td>Trivalent Chromium (mostly)</td>
</tr>
<tr>
<td>Painters</td>
<td>Trivalent Chromium and Hexavalent Chromium</td>
</tr>
<tr>
<td>Battery makers</td>
<td>Hexavalent Chromium</td>
</tr>
<tr>
<td>Candle makers</td>
<td>Trivalent Chromium and Hexavalent Chromium</td>
</tr>
<tr>
<td>Dye makers</td>
<td>Trivalent Chromium</td>
</tr>
<tr>
<td>Printers</td>
<td>Trivalent Chromium and Hexavalent Chromium</td>
</tr>
<tr>
<td>Rubber makers</td>
<td>Trivalent Chromium and Hexavalent Chromium</td>
</tr>
<tr>
<td>Cement workers</td>
<td>Trivalent Chromium and Hexavalent Chromium</td>
</tr>
<tr>
<td>Maintenance and servicing of copying machines, and the disposal of some toner powders</td>
<td>Hexavalent Chromium</td>
</tr>
</tbody>
</table>

**Chromium and its Forms**

Chromium metal does not occur naturally and is produced from chrome ore. Chromium is an odorless, tasteless, hard, lustrous metal with a steel-gray appearance and is available in crystal or powder form. The main industrial use of chrome metal is corrosion protection for automobiles and equipment accessories and in alloying elements in stainless steels. Chrome metal can also be used as a plated coating over fasteners for salt-water applications. It gives rubies and emeralds their color and is used in nuclear and high temperature research. Chromium is available most frequently in three oxidation states, which include metallic chromium, trivalent chromium, and hexavalent chromium.

Metallic chromium is not found in nature but produced through processing chrome ore. It is a steel-gray solid with a high melting point and is used to make steel and other alloys.

Trivalent chromium is used for chrome plating, dyes and pigments, leather tanning, and wood preserving. Smaller amounts are used in rust and corrosion inhibitors,
textiles, and toner for copying machines. It naturally occurs in rocks, soils, plants, animals and volcanic emissions. Chromium-rich foods include, beef, liver, eggs, chicken, oysters, wheat germ, brewer’s yeast, green peppers, apples, bananas, and spinach. In addition, black pepper, butter, and molasses are also good sources of chromium, but they are normally consumed only in small amounts. Trivalent chromium is believed to play a nutritional or pharmaceutical role in the human body, but its mechanism is still unknown. It is also believed to be an essential nutrient that helps the body use sugar, protein, and fat. The estimated safe and adequate daily intake of chromium for adults is in the range of 50 to 200 µg/day. A lack of chromium has been associated with atherosclerotic heart disease, elevated cholesterol levels in the blood, and high fat content in the aorta. Unfortunately, there is not sufficient data for the medical industry to establish a solid, recommended daily allowance.

Hexavalent chromium is the only toxic form that is currently known. It has proven to be one of the greatest occupational and environmental risks and is produced industrially when trivalent chromium is heated in the presence of mineral bases and atmospheric oxygen, for instance in the metal finishing process. Most commonly, this form of chromium is found in the two oxidized species, chromic acid (CrO₃) and chromates (CrO₄²⁻) which are strong oxidizers. In a solution, hexavalent chromium exists as hydro chromate (HCrO₄⁻), chromate (CrO₄²⁻), or dichromate (Cr₂O₇²⁻). The dichromate form is used in hot-dip galvanized quench baths and has been effectively used in a 0.15% wt. sodium chromate solution with a natural pH of 4.3. Chromium’s aggressive oxidizing behavior makes it an ideal product for an anti-corrosive coating, but this behavior may make it a dangerous health risk. Fortunately, hexavalent chromium rarely occurs in nature and only high amounts of it become present in the environment due to human activities. With all the benefits of chromate conversion coatings, some significant drawbacks arise in the realm of environmental and health.

**Exposure**

Adding to the gravity of the hexavalent chromium situation is its multiple routes of exposure. Exposure can take place through inhalation, oral ingestion, or dermal
contact. A person can be exposed to chromium by eating food grown in contaminated soil, drinking water with chromium present, breathing contaminated air, or direct contact with a material containing hexavalent chromium. In addition, a person can be exposed to chromium by living near uncontrolled hazardous waste sites containing chromium. All of these factors have led to organizations recently applying pressure on government agencies to regulate more stringent hexavalent chromium exposure limits.

**Ingestion**

The *11th Report on Carcinogens* indicates that typical tap water may contain up to 8.0 micrograms per liter (µg/L) of total chromium, and chromium levels in rivers and lakes usually fall between 1 and 10 µg/L. Hexavalent chromium by itself is not regulated in drinking water, merely the total chromium content of the water is regulated. Hexavalent chromium, by itself, is not regulated by the U.S. Environmental Protection Agency (EPA). The EPA has set a maximum contamination level for total chromium of 100 µg/L, but some states have set levels that are more stringent. Usually these levels are set at 50 µg/L, which is half of the EPA contamination limit.

Particles of chromium can be ingested if the dust gets on ones hands, clothing, or, and then transferred to food or beverages. Ingesting large amounts of hexavalent chromium can cause an upset stomach, ulcers, convulsions, kidney and liver damage, and even death. This observation became better known when Hollywood made the film entitled *Erin Brockovich*, which highlights one small California town’s battle with a negligent water utility. On December 7, 1987, officials from Pacific Gas and Electric Company (PG&E), the world's largest utility company, advised California regulatory authorities that they had detected hexavalent chromium at levels of 580 µg/L, over eleven times the state's 50 µg/L limit for total chromium, in a groundwater monitoring well. Hexavalent chromium was being used as an anti-corrosive in the cooling towers of a PG&E gas compressor station in the Mojave Desert town of Hinkley. This case remains controversial among chromium experts because most of the Hinkley exposures involved drinking hexavalent chromium-laced water. This route of exposure is widely believed to be less toxic than inhalation because ingested hexavalent chromium is converted to
trivalent chromium in the stomach. Many experts also claim that the exposures were too low to cause health effects and that there is not sufficient data linking hexavalent chromium exposures to the Hinkley residents' symptoms. But still others counter that there are too many gaps in the data on chromium to dismiss the Hinkley residents' case and they believe the fact that this toxic form of chromium can enter all types of cells. If true, scientists may yet discover that it can damage many human organs. Until more is known about how different doses and routes of exposure to hexavalent chromium affect different populations, it is too soon to rule out high drinking water exposures as a health risk.

**Dermal Contact**

Dermal contact with chromium compounds results in skin sensitization and dermatitis. Hexavalent chromium compounds are powerful skin irritants and can be corrosive. Dermal exposures may cause skin ulcers or allergic reactions because hexavalent chromium is one of the most highly allergenic metals, second only to nickel. In sensitized workers, allergic reactions consisting of severe redness and swelling of the skin. If skin encounters chromium, very little of it will enter the body unless the skin is damaged prior to contact with the chromium. On broken skin, a penetrating round ulcer may develop. A chrome sore begins as a pimple, forming an ulcer with raised rough edges. Ulcers may penetrate deep into soft tissue or become a site of a secondary infection. A “chrome hole” is not known to lead to cancer but the lesions heal slowly and may persist for months. Common sites for these ulcers or “chrome holes” include the nail root, knuckles, finger webs, back of hands, and forearms. Usually, workers handling liquids or solids that have high hexavalent chromium levels can develop skin ulcers from this exposure.

![Figure 1: Dermal contact with over exposure to hexavalent chromium](image)
In a work environment where chromate compounds are used, there is the possibility of exposure due to inhalation if these compounds can be transformed into mist, vapor, or fume forms. The air can become contaminated when mists of liquid containing hexavalent chromium are sprayed, when dust particles containing hexavalent chromium are dumped or swept, or when fume particles containing hexavalent chromium get into the air by melting or welding a metal that contains chromium. Hexavalent chromium can get on cigarettes and if a contaminated cigarette is smoked, the smoker inhales additional chromium along with the tobacco smoke. Hexavalent chromium is a respiratory tract irritant. When a person breathes hexavalent chromium, irritation will usually occur in the nose, throat, and the lungs. Repeated or prolonged exposure to hexavalent chromium can damage the mucous membranes of the nasal passages and can cause ulcers to form and, in some cases, the damage is so severe (see Figure 2) that a hole can develop in the wall separating the nasal passages known as the septum.

Breathing high levels of hexavalent chromium, greater than 2 µg/m³, such as fumes from compounds known as chromic acid or hexavalent chromium trioxide, can cause irritation to the nose, manifested as a runny nose, sneezing, itching, nosebleed, ulcer, and/or holes in the nasal septum. These effects have primarily occurred in factory workers who have produced or used hexavalent chromium for several months.

In North America the total chromium concentrations in the ambient air are typically less than 0.01 µg/m³ in rural areas and up to 0.03 µg/m³ in urban areas. At this time, the EPA does not regulate chromium in ambient air. Long-term exposure to hexavalent chromium has been associated with lung cancer in workers exposed to levels that were 100 to 1,000 times higher than those found in the typical environment.
cancer may occur long after exposure to chromium has ended. Inhaling amounts less than 2 µg/m$^3$ of hexavalent chromium for short or long periods of time does not appear to affect most people. However, high levels of chromium in the workplace have been known to cause asthma attacks in people who are allergic to chromium.

**Conversions of Hexavalent Chromium to Trivalent Chromium**

According to the Agency for Toxic Substances and Disease Registry (ATSDR), chromium enters the air, water, and soil mostly in the trivalent chromium and hexavalent chromium forms. In the air, chromium compounds are present mostly as fine dust particles that eventually settle over land and water. Chromium can strongly attach to soil allowing only a small amount to dissolve in water, which will help prevent it from moving deeper into the soil and into the underground water supply.

Soil, meanwhile, contains an average of 400,000 µg/L of total chromium, depending on the balance of oxidizing and reducing agents in the soil. In EPA's 1998 Toxicological Review, hexavalent chromium in the soil is reported to convert into trivalent chromium by dissolved organic matter. The levels of both trivalent chromium and hexavalent chromium in the soil increases mainly from disposal of commercial products containing chromium, coal ash from electric utilities, and chromium waste from industry.

According to the International Agency for Research on Cancer (IARC), ingested hexavalent chromium is largely converted to trivalent chromium in the stomach. Since trivalent chromium is not readily absorbed into the body, it does not pose a significant health risk. The saliva, gastric juice, intestinal bacteria, blood, liver, epithelial lining fluid, pulmonary alveolar macrophages, peripheral lung parynchema, and bronchial tree have all been associated with eliminating hexavalent chromium from the body. A study done in 1997 found that major detoxification is accomplished by red blood cells, with over half of a 100-microgram (µg) dose of hexavalent chromium being sequestered or reduced to trivalent chromium by 1 milliliter of blood within 60 minutes. In other studies, it has been noted that as much as 10% of hexavalent chromium is absorbed following oral consumption and may remain in the human body for up to five years.
Hexavalent chromium has a chemical structure similar to phosphate, which is transported into all types of cells. Once hexavalent chromium enters a cell, it is chemically transformed to trivalent chromium. However, this does not mean that the cell is necessarily safe from adverse effects. Inside a cell, trivalent chromium has the capacity to damage DNA. Research by Karen Wetterhahn, a chemist at Dartmouth Medical School in Hanover, New Hampshire, states that the uptake and reduction of hexavalent chromium by cells, indicated that it acts as a "trojan horse" for delivering DNA-damaging trivalent chromium into cells.

Effects

It has been more than 80 years since it was first observed that workers in the German chrome industry developed lung cancer more often than the rest of the general population. Several studies have shown hexavalent chromium compounds can increase the risk of cancer. The World Health Organization (WHO), the Department of Health and Human Services, and the EPA have determined hexavalent chromium as a breathable dust to be a carcinogen in humans, although the EPA has also determined that there is insufficient information to determine whether hexavalent chromium in water or food or trivalent chromium are human carcinogens as well.

Risk Factors

If a person is exposed to chromium, many factors determine whether he/she will be harmed and how severe the case could become. These include the duration of the contact, the form of hexavalent chromium, and the exposure quantity. Another factor is the effect of other chemicals he/she are working around. This plays a part because their lungs could already be irritated by the acid used in the pickling tank and a new irritant (e.g. chromium) could be introduced that could be more harmful since the body is already fighting off the first irritant. Finally, some other individual factors include age, gender, and diet. Employees may be exposed to higher-than-normal levels of chromium if they live near any of the following: landfill sites with chromium-containing wastes; industrial facilities that manufacture or use chromium and chromium-containing compounds;
cement-producing plants because cement contains chromium; industrial cooling towers that previously used chromium as a rust inhibitor; waterways that receive industrial discharges from electroplating, leather tanning, and textile industries; or busy roadways, because emissions from automobile brake lining and catalytic converters contain chromium.

**Testing Procedures**

There are three ways to test for chromium in the workplace. The first test that can be done is an air monitoring test to ensure the quality of the air. The test procedures can be found at [http://www.osha.gov/dts/sltc/methods/inorganic/id215/id215.html](http://www.osha.gov/dts/sltc/methods/inorganic/id215/id215.html). A second is a wipe test. This test can be performed on a product once it has been removed from the quench bath. The wipe test method can be found at [http://www.osha.gov/dts/sltc/methods/validated/t-w4001-fv-02-0104-m/t-w4001-fv-02-0104-m.html](http://www.osha.gov/dts/sltc/methods/validated/t-w4001-fv-02-0104-m/t-w4001-fv-02-0104-m.html). The air monitoring and wipe tests are OSHA recommended and can be performed by a qualified lab. The third and most common test for human exposure to toxic metals is done by determining the concentrations in their blood, hair and urine. These tests are most useful for people who have been exposed to high levels of chromium. These tests cannot determine the exact levels of chromium that one may have been exposed to or predict how the levels in the tissue will affect health. Since trivalent chromium is an essential element and naturally occurs in food, there will always be some level of chromium in the body. High chromium levels in the urine and red blood cells indicate exposure to hexavalent chromium or trivalent chromium compounds, since the body changes hexavalent chromium to trivalent chromium. The form of chromium that one was exposed to cannot be determined from the levels in the urine or blood. Much more hexavalent chromium can enter red blood cells than trivalent chromium, but hexavalent chromium can be changed to trivalent chromium within these cells. Therefore, chromium levels in the red blood cells indicate exposure to hexavalent chromium. Since red blood cells last about 120 days before they are replaced by new ones, the presence of chromium in red blood cells can show whether a person was
exposed to chromium 120 days prior to testing but not if exposure occurred longer than 120 days before testing.

Reducing Exposure

The two best methods of reducing the exposure to hexavalent chromium are through substitution of hexavalent chromium with an alternative in the metals process or through engineering controls on the chromium process in the plant. If chromium-free substitutions in the process are not possible, then one engineering control system that is easy to install is the local exhaust ventilation (LEV) system. A mechanically powered local exhaust hood can be placed at the point where chromium is released into the air, or the entire process can be contained within the hood. Properly designed and maintained local exhaust ventilation (LEV) removes most of the chromium compounds before they can be inhaled. Using an LEV is much better than leaving doors and windows open, or bringing in fresh air through a fan or duct. With dilution or general ventilation, overexposure can still occur at the point where the chromium compounds are released into the air, or where the diluted air does not mix well with the room air and has concentrated levels of chromium compounds. Two other engineering options are the use of personal protective equipment (PPE) and safe work practices. Some appropriate PPE’s for chromium processes are: splash proof goggles, face shield, chemical resistant gloves, apron, boots, paper dust mask (designed to remove powder and mist particles created during chrome plating). A respirator, which is the least effective way to control exposure, should only be used as a last resort since it is most commonly used improperly. Safe work practices can consist of no eating, drinking or smoking in the workplace and washing hands and face before eating, drinking, or smoking.

Chromate Passivation

The use of a quench containing hexavalent chromium compounds in solution has been a traditional treatment for passivating the raw, reactive zinc surface on freshly galvanized steel. Fresh zinc is highly reactive. In fact, the corrosion products that form on the surface over time provide galvanized steel with its superior corrosion protection.
The mild corrosion products formed in the natural weathering process of galvanized steel create the tight barrier coating known as the zinc patina. Problems can arise, however, before the patina has formed, if the newly galvanized materials are not stored properly.

When newly galvanized steel is shipped or stored in closely packed, stagnant, or humid environments, conditions exist for the generation of voluminous white corrosion products that are commonly referred to as wet storage stain. In extreme cases, under certain storage practices, these untreated products can become severe, with significant wet storage stain buildup and even red rust. These detrimental corrosion products can require either removal and repair, stripping and re-galvanizing, or can even render the steel unusable for the intended application.

One way of preventing the build-up of excessive corrosion products, is to quench the recently galvanized materials in a chromate bath. Hexavalent chromium treatments, commonly called chromate conversion coatings, have been shown to effectively impede the corrosion reactions that generate wet storage staining. Metals that contact chromate ions in solution undergo a surface reaction. During this reaction, some of the hexavalent chromium is reduced to trivalent chromium, forming a complex gel on the metal surface.

The initial stage in the formation of a chromate passivation layer is dissolution, which releases both zinc and hydrogen from the coating surface. This chromate passivation coating contains trivalent chromium with some hexavalent chromium compounds mixed in. The remaining hexavalent chromium from the passivation coating is absorbed into the top coat.

This gel-like coating contains both trivalent and hexavalent chromate ions and is soft, porous and absorbent. Additionally, the coating may add color to the galvanized steel. Color can range from nearly clear to yellow, green, brown, olive, or black. The thicker the coating, the darker the resulting color. Typically, galvanizers provide thin conversion coatings with only a hint of color. These thin coatings provide only temporary protection against wet-storage stain and typically remain for six weeks to six months.

Hexavalent compounds provide a unique self-healing ability. When damaged, soluble hexavalent chromium compounds contained within the passivation films will
repassivate any exposed areas. Small scratches and surface abrasions will still retain the passive qualities of the applied film.

The type of chromate conversion coating used for prevention of wet storage stain is intended solely for passivating the reactive zinc surface and can interfere with adhesion if the fabrication is intended to be painted.

**Reinforcing Steel**

In freshly poured cement, raw zinc reacts to form stable, insoluble zinc salts accompanied by hydrogen gas. The hydrogen gas produced in this reaction, if in large enough quantity, can leave voids in the concrete as it makes its way to the concrete’s surface. If the voiding is significant, the concrete bonding strength is compromised, rendering the fabrication unsatisfactory for use in construction. However, this situation is not always observed because in practice, the surface of galvanized steel is not raw. Typically, some time has elapsed between when the product especially rebar was initially hot-dip galvanized and when it reaches the construction site. During this period, fresh zinc reacts with its surroundings to form the passive products called the protective zinc patina. Likewise, during the transportation to the construction site and storage at the construction site, some of these same passive corrosion products can form, thus limiting the raw reactive zinc exposed to the concrete pour, and consequently limiting some of the hydrogen evolution reaction. As a precaution, ASTM 767 recommends using a chromate quench to apply a passivation film on the surface of the rebar that retards this hydrogen producing reaction. Another method involves adding chromate mixtures to the concrete that effectively eliminates the hydrogen producing reaction. According to ASTM 767, a chromate quench bath should contain at least 0.2% of sodium dichromate or chromic acid, in a solution of water. In a galvanizing plant, inhalation could take place from working near the chromate quench tank; however, a dangerous level of exposure has not been reported at this time.

**Industry Data**
In Figure 3, results are shown from a few plants that tested employees for total chromium levels in their blood. The heavy dark grey line is the lower reference limit and the thin grey line is upper reference limit, which are set by each lab based on EPA standards. These limits are predetermined as a safe allowable limit for an employee to have in their system. The black line is the detection limit that is the lowest detectable amount of chromium that can be tested in a blood sample from an individual. The dashed line is an average of the chromium found in the employees that work in a galvanizing plant that does not use chromium quench. As you can see, all of the data, except one sample, falls below the upper reference limit. The sample result above the upper reference limit is a possible sign of overexposure. More testing and more information about other contributing factors concerning this individual is recommended to ensure the quality of the test information and to determine if this result is a one time occurrence or not. This potential exposure in the industrial setting should be investigated, as well as the potential for exposure from some other source of chromium.

**Figure 3: Graph of chromium levels in galvanizing plants**

In Figure 4, the measured total chromium levels present in the air in galvanizing plants with a chromate quench bath are shown. The squares represent total chromium for each plant. As the graph shows, the average of the measured data are well below the OSHA Permissible Exposure Limit (PEL) for hexavalent chromium and the measured data includes all forms of chromium compounds.
Figure 4: Air monitoring data for total chromium from galvanizing plants compared to OSHA PEL for hexavalent chromium.

In Figure 5, the same data from the Figure 4 is shown compared to the proposed OSHA PEL limit for hexavalent chromium. The average dashed line for all of the measured plant data is now above the solid line, representing the proposed limit. This means that more testing needs to be done in these plants to isolate hexavalent chromium from the total chromium samples since the samples when testing.

Figure 5: Air monitoring data for total chromium from galvanizing plants compared to OSHA PROPOSED PEL for hexavalent chromium.

According to the existing OSHA PEL the galvanizing industry is not at risk at this time. In addition, there have not been any cases reported of chromate related injuries or illnesses in galvanizing operations, even though chromate quenching baths have been used for many years in the galvanizing industry. With the possibility of OSHA lowering
the PEL for hexavalent chromium, the industry will need to do more testing since the only data that is available for air concentration measurement is total chromium levels.

**Chromate Alternatives**

With the possibility of chromium being phased out of industries in other parts of the world, alternatives to chromium quench are being developed. Research is being conducted on the use of molybdenum compounds as an alternative to hexavalent chromium. Molybdates were first tried because they belong to the same group in the periodic table as chromium and are known to have low toxic action in the environment, proven by their long-term use as corrosion inhibitors. Results from a Chinese study show similar corrosion rates to chromate coatings. In the literature review for ILZRO project ZCO-26 “White Rust Prevention”, it was noted that these compounds immediately alter the end-products appearance completely suppressing the glossy appearance. Therefore molybdates were not chosen for the final testing phase in that project. Chromate alternatives were selected based on the following primary and secondary criteria:

**Primary**
1. Nontoxic
2. Water Soluble
3. Readily Available
4. Maintains Original Appearance
5. Environmentally Safe
6. Used in Single Tank, less important

**Secondary**
1. Low Cost
2. Easily Painted Over
3. Easily Controlled and Maintained

These criteria were evaluated by performing various tests to measure the following behaviors:
1. Outdoor Exposure (coastal, rural, and industrial)
2. Resistance to Thermal Shock
3. Influence of Pollution

4. Adhesion Property of the Duplex System

The study concluded that based on the above criteria only two products performed acceptably. “Zaclon WRP gave very good results when the temperature of the treated material is between 150 and 230°C.” This narrow operating range was cited as the largest drawback and thus making it nearly impossible to use a single quench effectively with a wide array of steel material thicknesses. The report states that a two-step treatment where the material is first quenched and then passivated in a 60°C bath is the optimum solution but clearly inferior to the best conditions. Another product, Gardo TP 10342 from Chemetall GmbH, also met the requirements as the best overall performer in the outdoor exposure tests. It can be used directly in the quench tanks, but evolves NH₃ during passivation. Nevertheless, until removal of chromium is mandated, the switch to non-chromate alternatives for passivation is not attractive.

The 1997 American Galvanizers Association Process Survey reported that 35 of 117 plants used chromates in the quench bath. According to the most recent data, 2003 American Galvanizers Association Process Survey, chromate quench use has stayed constant, with 24 of the reporting 62 plants currently using a quench tank with chromate additives. No other non-chromium quench additives were reported. Alternatives to chromates are being researched throughout the world due to the negative environmental aspects of utilizing chromates in industry. However, no commercially acceptable alternative that possess the excellent zinc passivation properties of chromates has been found yet.

According to the OSHA PEL, the galvanizing industry is not at risk at this time. In addition, there have not been any cases reported of severe chromate related injuries or illnesses. With the possibility of OSHA lowering the PEL for hexavalent chromium the industry will need to do more testing since the only data that we have is for total chromium. As of today, only lung cancer has been linked with occupational chromium exposure.
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