Advice & Counsel

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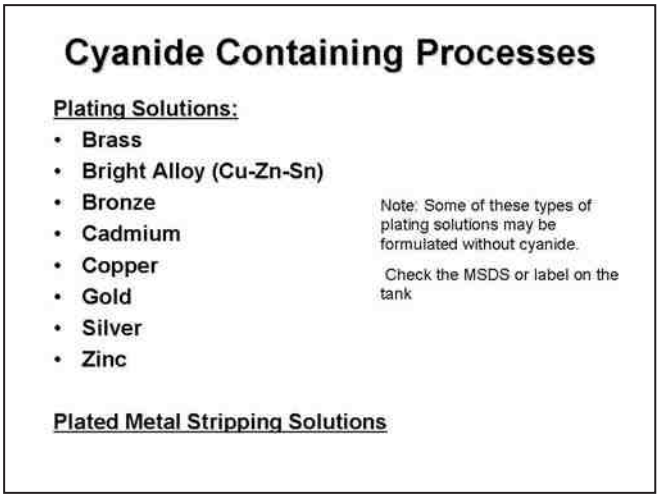
Cyanide Safety

Dear Advice & Counsel,

My company has recently installed a metal stripping process that utilizes cyanide-containing proprietary product. I am not familiar with how to use cyanide safely and would like some basic cyanide safety information. Can you help?

Signed,
Casey Enn



Dear Casey,

I will provide you with the basics of cyanide safety, but I must caution anyone reading this and any following articles on the topic, that cyanide safety is discussed here in a general manner. Your specific process may have safety issues that will not be covered here, so don't count on this as a "complete" discussion of the issues. Also, I am not a doctor, so any information given here is not an attempt at practicing medicine. Check with your own doctor for a specific diagnosis.

First, let me state that cyanide has been used in metal finishing for over 150 years, and the number of casualties related to accidental poisoning with cyanide in an industrial setting is relatively low.

During my career, I have only heard/read of a handful of workers dying from cyanide poisoning. In many of these cases, the poisoning was self inflicted (suicide) or the result of extreme carelessness. For example, several workers were killed when one of them added concentrated acid to a cyanide containing crust on an empty tank during clean-up.

Cyanide can be and is being used in the metal finishing industry on a daily basis, with a high level of safety.

Cyanide basics

Cyanide is an anion that is a combination of one carbon and one nitrogen atom (CN). Carbon and nitrogen are relatively harmless chemical elements, but when they are combined in this atomic ratio, a potentially deadly anion is produced. Cyanide-ion containing compounds are commercially produced and more than 90% of worldwide production is used in the mining industry. Only a very small percentage is used in metal finishing.

Nature also produces cyanide, as some bacteria, fungi and algae produce cyanide as a by-product as they live and die. Certain plants such as peach pits, almonds, spinach, tapioca and bluegrass contain naturally produced (very low concentrations) of cyanide compounds.

Cyanide-containing compounds fall into two broad categories: simple and complex.

Simple cyanides

In general, simple cyanides are considered to be highly toxic and relatively unstable, especially when acidified or combined with oxidizers, while complex cyanides have higher levels of stability and may have lower levels toxicity, depending on the composition.

Simple cyanide examples are potassium and sodium cyanide (KCN and NaCN). These are the most commonly encountered cyanide compounds in metal finishing. Sodium and potassium cyanide are white crystalline compounds that may also be compressed into more easy-to-handle shapes such as "eggs" or "briquettes." These compounds give off a bitter almond "nutty" smell, but not everyone has the ability to detect this odor.

Sodium and potassium cyanide are easily dissolved in water and are highly toxic via ingestion. As little as 6.4 mg/kg of body weight kills 50% of a rat population in experimental investigations. That is equivalent to a 220-pound man ingesting only 0.64 grams or 0.02 ounces.

Hydrogen cyanide may also be considered a simple cyanide. It is a gas that is produced by accidentally mixing acid or an oxidizer and simple or complex cyanide. Hydrogen cyanide is not intentionally used in metal finishing. It is a colorless gas that also has a weak bitter almond smell, but again, not everyone can detect this odor.

Complex cyanides

In general, complex cyanides tend to be stable and many are not soluble in water. Complex cyanide compounds tend to resist decomposition upon the addition of acid and do not readily produce hydrogen cyanide unless the acid added is strong or the complex compound is heated to high temperatures. Some complex cyanides are so stable and low in toxicity that they have been used to color blue-jeans and as anti-caking agents for road salt.

Examples of complex cyanides are potassium ferricyanide ($K_3Fe[CN]_6$) and potassium gold cyanide ($KAu[CN]_2$). There are many dozens of complex cyanide-containing chemical compounds, but only a few are utilized in the metal finishing industry.

Uses of cyanide in metal finishing

In metal finishing, the most common processes that employ cyanide ions are electroplating and stripping operations, some of which are listed in Table 1. In electroplating solutions, sodium or potassium cyanide may be included in the process formulation to allow alloy deposition, improve solution conductivity, control metallic impurities and dissolve metallic anodes.

In stripping solutions, sodium or potassium cyanide is utilized to chemically combine with the metal being stripped, resulting in the dissolution of the plated metallic layers. By the incorporation of suitable inhibiting agents, these stripping solutions are fast, operate at room temperature and maintain their speed of stripping for a long time. It should be noted, however, that all stripping solutions are not necessarily formulated with cyanide.

Health issues

Exposure routes

Cyanide poisoning may result from exposure via several routes, but inhalation and ingestion are the most common ones.

Inhalation

There are two physical forms of cyanide-bearing air emissions that are possible from metal finishing processes containing-cyanide; particulate and gas. Particulates containing cyanide are typically mists that may be produced by gases or air bubbles bursting at the surface of a process solution. Under most circumstances, these emissions are captured and removed from the air stream by exhaust and scrubbing systems.

Most metal finishing processes containing simple cyanides are stabilized by the addition of large amounts of alkalis such as sodium or potassium hydroxide, so there is little if any possibility of gaseous hydrogen cyanide being formed due to decomposition.

NIOSH studied particulate emissions on several cyanide containing electroplating solutions in 1984 (NIOSH publication 85-102) and found that in general, personal exposure to particulate cyanide emissions were below detection in ventilated and unventilated electroplating tanks.

The main inhalation danger is from accidental mixing of any acidic solution and a cyanide-containing solution, yielding gaseous hydrogen cyanide. Industrial fires in metal finishing shops can also release cyanide gases. Inhalation of smoke from such a fire can result in cyanide exposure.

Workers who smoke cigarettes routinely expose themselves to long-term exposures of low concentrations of cyanide (note the Surgeon General's warning on packs of cigarettes). Such long-term exposures may increase the vulnerability of smokers to cyanide toxicity and can cause some of the symptoms of over-exposure noted below.

Ingestion

Ingestion of cyanide-containing compounds is typically a result of carelessness on the part of the worker. Failure to utilize appropriate personal protective equipment (PPE) or failure to wash hands before eating or smoking can result in the ingestion of cyanide-containing materials.

Skin/eye contact

Cyanide may be absorbed through the skin or membranes of the eye. Therefore, use of protective gloves, goggles (face shield if splashing or dust exposure is a possibility), boots, eye protection and impervious clothing is very important when working with these compounds and solutions.

Health effects

The primary mechanism by which cyanide impairs the proper function of internal organs is the combination of cyanide with the hemoglobin in the blood stream. This prevents hemoglobin from properly oxygenation bodily cells, effectively starving the organs of oxygen. Cyanide-bearing solutions are also highly caustic, producing chemical burns upon skin contact, inhalation or ingestion.

The route of exposure to cyanide does not change the health effects/symptoms of cyanide poisoning to any significant degree, with the exception of skin contact. Exposure through skin contact may result in sores and rashes of the skin. Symptoms similar to inhalation and ingestion may be slower to show when the route is skin contact.

Signs of low level exposure to cyanide include the skin turning pink to red. High levels of exposure may turn the skin blue. Reddening of the eyes and pupil dilation may be evident.

Exposure to high concentrations of airborne or ingested cyanide can impair the proper function of numerous organs, including the liver, kidneys, heart and central nervous system, and can cause coma and death.

OSHA regulates worker exposure to inhaled cyanide at 5 mg/m^3 of air on an 8-hour time-weighted average.

Ingestion of cyanide typically results in rapid deep breathing/shortness of breath. If the ingestion is above the toxic amount, convulsions, loss of consciousness and death can result in a matter of minutes.

Exposure to cyanide at levels that are not toxic may still cause serious health effects including breathing problems, chest pain, headaches, damage to the thyroid gland and gastric irritation.

To the best of my knowledge, long term exposure to cyanide has not been linked to cancer or birth defects.

Antidote for cyanide poisoning

OSHA requires an employer to have on hand first aid for any foreseeable injury. There is a first aid "kit" available (manufactured by Eli-Lilly and available only by prescription from a licensed doctor) that includes the chemicals and equipment needed for first aid response. The kit has detailed instructions for first aid response.

Except for the pearls of amyl nitrite, the kit contents are designed and intended for use by a medical professional. However, since time is of the essence in a cyanide incident, workers should be trained on how to utilize the amyl nitrite pearls in an emergency. To avoid abuse of amyl nitrite, it should be stored in a "break glass" box. The pearls should not be locked up, as that would inhibit rapid response. ***P&SF***