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Alternatives for Hex Chrome Exposure Standard

On February 28 of this year OSHA published the new regulations concerning exposure to hexavalent chromium. This information is described in the *Federal Register*. What is important from this new standard is the following federal mandated requirement:

The PEL (permissible exposure limit) for hexavalent chromium and all other hexavalent chromium compounds is five micrograms per cubic meter of air as an eight hour time-weighted average.

By comparison, the previous limit was 52 micrograms per cubic meter of air for the same eight hour time-weighted average. The new regulation cuts the exposure limit by a factor of 10. Initially, OSHA did propose the PEL limit for hexavalent chromium to be reduced from the old 52 limit to only one microgram per cubic meter of air. That would have been a reduction requirement of 50 times. However, OSHA, upon more undertaken studies, determined that a low of five micrograms per liter of air would be realistically feasible. They based this conclusion on the fact that technological capabilities in an economic reality could meet the five value. This new PEL limit of five may not stick, however. The Public Health Citizen Group announced they would sue OSHA, claiming the new five PEL is not low enough. For the time being, we can acknowledge that five micrograms per cubic meter of air is the standard to meet.

Avoiding acute health and safety related issues toward hexavalent chromium exposure has been of the highest priority in the metal finishing industry. With regards to hexavalent chromium, this became especially important in 1971. That is the year that several government agencies (such as EPA, NIOSH) declared that hexavalent chromium compounds cause, or may cause, lung cancer in exposed workers. Protective measures for personnel have included special clothing and respiration filters. Examples of these are: coveralls, face shields, filter masks, respirators, and gloves. Equipment upgrades, such as, exhaust ventilation, process tank covers, and air filtration (work floor and at stack) have also been maintained. Chemistry and process tank improvements have included the implementation of fume suppressants, less concentrated hexavalent chrome containing systems, and the introduction of trivalent chromium process alternatives. The new hexavalent chromium PEL will certainly result in upgrades to the forms of personnel protective items just listed, and either replacements or alternatives to some traditional hexavalent chromium baths. Let us review some subjects in motion with regards to changes in hexavalent processes and suitably operating alternatives.

Hexavalent Chromium

Simply stated, hexavalent chromium is just that, nothing more or less. For decades compounds containing hexavalent chromium have been the "nothing does it better" systems in metal finishing. Plating (decorative and hard), chromating, passivation, and rust inhibition, have been major contributions by hexavalent chromium containing compounds. In decorative and hard chrome plating, fume suppressants have been improving as new, more effective, longer lasting agents, are used in formulations. Mist and fume suppression can routinely be over 99.99 percent effective when using mist and fume suppressants as recommended. This also relates to much less exposure of plating equipment and ventilation systems to corrosive mists and fumes.

Hexavalent chromium plating baths have typically been 10–15 percent efficient with respect to chrome deposition. The development of different catalysts, blends as mixed double and triple catalyzed systems, have improved decorative efficiency. Mixed catalyzed hard chrome baths have markedly increased plating speed. These baths can plate up to four times faster than conventional chrome baths.

Chromates have not changed to any great extent. Clear (blue), yellow/iridescent, bronze, olive, green, and black, still retain time tested and acknowledged formulations. Used per recommendation over properly plated parts (or base metal), these processes long ago set the current salt spray and other corrosion test requirements.

There has been a steady progression towards using more of the hexavalent chrome containing liquid concentrated products. The main reason is the elimination of dustiness in handling. It goes a long way to help meet the chrome five PEL.

Trivalent Chromium

These processes have been developed chiefly to counter the negative, or detrimental points associated with hexavalent chromium. Among these are: carcinogenic classification of hexavalent containing compounds, extremely corrosive, strong and potentially hazardous oxidative strength, and poor chrome plating efficiency. Effective trivalent systems include decorative plating and chromates. Trivalent chromium containing compounds are non-carcinogenic, at most mildly corrosive, and their use in metal finishing is actually favored by federal health and safety organizations. In fact, as a health issue, over the counter multiple vitamins contain a trivalent chromium compound. It is very important to note that trivalent plating and chromates offer major process advantages in the current international market. Trivalent systems meet the End-of-Vehicle Life (ELV) requirements and RoHS directives. For the user, trivalent process baths offer a large in-house benefit. This is the ease of waste treatment.

Most trivalent baths contain less chrome than the similar hexavalent one. The chrome, being trivalent, only needs to be alkaline precipitated.

Trivalent chromium plating is typically 30 percent efficient (twice that of hexavalent chromium). There is much less misting of non-corrosive solution. The deposit is normally slightly darker compared to the traditional hexavalent deposit, to a pewter like finish. Commercially, trivalent chrome plating is strictly for decorative or flash deposits. This is because the deposit is self limiting, not able to meet the requirements for hard chrome thicknesses. On-going work is being conducted to provide a functioning hard trivalent chrome bath.

Trivalent chromates are universally provided as liquid product concentrates. Clear trivalent chromates have been available, as commercially functioning processes, for over 20 years. Their operating parameters are similar to the hexavalent chromate. Chromated parts typically exhibit a darker tint of blue color versus the hexavalent color. Salt spray protection is similar. But, the trivalent bath has a greater tolerance to metallic contaminants. Therefore, trivalent clear chromate baths can run up to 3–5 times longer than clear hexavalent baths. This is based on the ability to meet salt spray specification. Trivalent chromates can also tolerate higher initial drying temperatures. In some instances this was found to improve corrosion resistance and deepen the blue deposit color.

Trivalent yellow chromates are different in operating parameters, as the working bath temperature range is from 130–175°F (54–79°C). The deposit color seems to favor a green hue. This can be "yellowed" by post immersion in a suitable dye. Trivalent black chromates are now becoming commercial. Trivalent clear and yellow chromates over aluminum have been in commercial use, meeting specific salt spray and MIL specifications. Green and bronze are still locked into hexavalent chromates.

Although the hexavalent chrome PEL has been reduced, hexavalent processes can still be used, under proper operating and maintenance conditions, meeting health and safety requirements. Trivalent processes offer a suitable, equivalent, or improved metal finishing treatment versus some hexavalent chromium systems. ***P&SF***

Author's note: I would like to recognize Chester M. Alter, PhD, who recently died. Dr. Alter, as a graduate student in the 1920s and 1930s, pursued research in electrochemistry. He was one of the earliest investigators of chromium electroplating.

In Memoriam

Steven Baker, 81, of West Newton, MA and Carefree, AZ died on March 22, 2006, following a short illnesss. He and is brother, Bob, founded Baker Bros., Inc., in 1950 and pioneered the use of programmed plating automation in North American in the early 1960s. Steven Baker was also responsible for the purchase of a small Dutch filtration company, Mefiag, and the Hanson Van Winkle Munning return-type plating systems.

After retiring, Baker was the head of the board of Visitors of the Boston University Hospital, and a member of the Harvard HILR, where he taught and took courses in a variety of subjects.

Baker is susrvived by his wife of 61 years, Shirley, a daughter, Joanne, and two sons, Neil of Pacific Palisades, CA (president of Baker Technology Associates and a joint venture partner with Asmega, sPa), and Michael, owner of Baker's Best, a large restaurant/caterer in the Boston area. Both sons spent years working with Baker Bros./ Systems.

Robert H. Shoemaker, chairman of the board of Kolene Corporation, Detroit, MI, died April 6, 2006, in Naples, FL, following a short illness.

Shoemaker graduated from Ohio University in 1943 and served as a Captain in the U.S. Marine Corp during World War II. He bagan working with Kolene in 1940 and rejoined the company in 1946 following college and military service.

Over the ensuing years, he and his father, John H. Shoemaker, extablished Kolene as the an international leader and innovator in the use of molten salt bath technology for industrail appliations, ranging from casting claning for military ships to coatigs removal and stainless steel procesing.

Robert H. Shoemaker succeded his father as president of the company in 1969. He served until 1988, when his son, Roger L., took over as president. He served as chairman of the board until his death.

During his career, Shoemaker was active in numerous industry associations, including ASM International where he served a president in 1976.

Besides his son, Roger, his is survived by his wife, Lois, and son Richard.

Lewis Midgley Walker, 88, of James Island, SC, died January 8, 2006 following a long illness. Walker was founder, president and CEO of Roll Technology Corporation, Greenville, SC, from 1972 to 1986. He served as chairman of the board from 1986 until 1992.

Walker served on the boards of the NAMF, the AESF Palmetto Branch, and the Southeastern Association of Metal Finishers. He also served on the board of the Greenville Chamber of Commerce. During his career, Walker received several lprofessional awards, including the Award of Merit from NAMF.

After World War II, he began his career in metal finishhing with Chromium Corporation of America in Waerbury, CN. He served as president of U.S. Metal Coatings Company in Middlesex,NJ, from 1952 to 1968. He remained active with the U.S. Naval Reserves for 23 years, retiring as a Commander.

Walker is survived by his wife, Ruth, and children Sharon W. (Gordon) Boyd of Saratoga Springs, NY; Lewis M. (Leigh) Walker III of Greenville, SC; Geoffrey H. Walker of Pheonix, AZ; and June A. (Nathaniel) Rodman of Chapel Hill, NC, and two grandchildren.

Answers to I.Q. Quiz #419

1. 25.4 lb. (Don't forget the $5H_2O$ in $CuSO_4 \cdot 5H_2O$)
2. 25.3 lb.
3. None, we hope.
4. 20.9 lb. (Don't forget the $7H_2O$ in $NiSO_4 \cdot 7H_2O$)
5. 24.7 lb. (Don't forget the $6H_2O$ in $NiCl_2 \cdot 6H_2O$)
6. 56.0 lb.